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By E. P. WOHLFARTH

Department of Mathematics, Imperial College, London

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## § 1. INTRODUCTION

HARD magnetic materials may be defined as substances with a high coercive force, say above 100 oersted. If such materials also possess high remanent magnetization they have innumerable uses as permanent magnet materials. For this reason an enormous body of experimental and theoretical research has grown up, and many spectacular advances have been made over the last 30 years or so, not least in the very recent past. It seems not unlikely that the immediate future will see a consolidation of this state of affairs rather than a continuation of rapid progress. For this reason a review of past achievement may not be inappropriate at this time, and such a review is presented in what follows.

Apologies seem to be in order for a number of reasons, both for the omission of many excellent papers, either deliberately or out of ignorance, and also for the commission of errors both subtle and blatant for which the author's lack of encyclopaedic knowledge should be blamed, though not, it is hoped, too vociferously.

Many other reviews of this subject have been published over the years. It suffices to mention the books of Bozorth (1951 b) and Vonsovsky (1956), the last giving an enthusiastic account of Russian achievements, and the articles of Hoselitz (1951), Dammöhl (1953) and Edwards (1957), the last including the most complete list of commercial permanent magnet materials. The present article is rather longer than average and aims at presenting the subject matter from a more unified point of view, including discussion of materials which do not seem to have immediate technological applications.



The present theoretical situation is outlined in § 2. The direct application of fine particle theory is to the properties of metallic and oxidic powder materials, as discussed in §§ 3 and 4. In § 5 there is a description of the behaviour of magnetically hard ferrites, and in §§ 6, 7 and 8 of magnetic alloys. The most blatant of the errors of omission just foreshadowed concerns the absence of any mention of thin films. Not only is research in this field in a state of great advance at this time, so that a rounded review would be difficult, but the more important developments are in the field of soft square loop materials and thus outside the present scope.

Grateful acknowledgments are due to all those who kindly sent preprints and reprints of their papers and to those who gave permission to reproduce diagrams and photographs.

## § 2. THEORETICAL

### 2.1. *Introductory: Brief Review of Theory of Domain Wall Motion*

The theory of the properties of magnetically hard materials is concerned primarily with interpretations of their high coercive force and, where applicable, of the anisotropy produced by magnetic annealing. Very roughly, the theoretical treatments proposed so far may be divided into two unequal groups. The first of these concerns domain wall motion as the principal magnetization process, but here little quantitative progress has been made in the field of high coercivity substances. The second group is concerned with rotational processes in small strongly magnetic particles, present either as physically distinct entities as in powder magnets or as precipitates in heterogeneous alloys. In this second group considerable progress has been made and this section is intended mainly as a review of fine particle theory (see also Wohlfarth 1956, Paine 1957).

The point of view that domain wall motions determine the hysteretic properties of magnetic materials, held particularly strongly in the 1930's, has been reviewed by Becker and Döring (1939). The problem concerns the field required to move a domain wall against the impeding irregularities such as internal stress variations which give rise to a positional dependence of the wall energy. By considering various reasonable modes of the stress variations it was found that the coercive force reaches a maximum value about  $\lambda\sigma/I_0$  if the wavelength of these variations is of the order of the width of the wall, where  $\lambda$  is the isotropic magnetostriction constant,  $\sigma$  the stress amplitude and  $I_0$  the saturation magnetization. To interpret the high coercivity of some materials very large values of  $\sigma$  have to be assumed and this is not always reasonable especially if, as may happen, the material is malleable and ductile (e.g. Cu-Ni-Fe alloys, cf. § 8). In other cases (cf. Nesbitt 1950, Kussmann and v. Rittberg 1950 a) high coercivity is accompanied by low  $\lambda$  and the above formula is inapplicable. Geisler (1953) ascribed magnetic hardness in some materials to coherency strains associated with precipitation but, although this idea is sometimes physically plausible, it seems difficult to develop quantitatively.

An extension of this approach was made by Kersten (1943) who considered variations in wall energy as being due to spatial changes of wall area due, for example, to the presence of non-magnetic inclusions. The quantitative results of Kersten's treatment seem to give reasonable agreement for magnetically quite soft materials such as carbon steels, but cannot sensibly be extended to high coercive force materials.

Later Néel (1946, cf. also 1949 a) was able to show that both the above approaches should be regarded as incorrect due to the neglect of magneto-static energy variations in a heterogeneous material containing impurities or stress variations. In such a substance the divergence of the magnetization vector does not vanish, and the energy associated with the 'disperse fields' due to the free magnetic poles can vary spatially. This variation gives rise to coercive forces of the order of those observed in relatively soft steels. The mathematical development of Néel's theory is rather abstruse and the validity of his results, relating coercive force to the volume of inclusions, the internal stresses and the effective volumes where these stresses can act, is even now not certain. Lilley (1952) showed that, in Néel's analysis, the stress distribution assumed is not, as was intended, a random one, but rather one in which large stress gradients are allowed at some points of the material, leading to inordinately large coercivities. For a more random distribution, these would be reduced, and Lilley considered spatially sinusoidal variations both of the direction of a constant amplitude stress and also of the amplitude of a stress of constant direction. The coercivities of ordinary soft magnetic metals may be accounted for on this basis without assuming extreme internal stresses. He also points out that the secondary domain structure, associated, for example, with imperfections, which is neglected in this and Néel's work, may have an important influence on the coercive force.

Vicena (1954) showed that the effects of wall energy variations may be quite important particularly for iron under the influence of internal stresses. For materials containing spherical non-magnetic inclusions Vicena (1955 a) found that the coercive force is determined primarily by the effects of the magnetic pole distributions on the surfaces of the foreign bodies, and for materials which are imperfect due to the presence of dislocations the coercive force is influenced (Vicena 1955 b) by the stress fields surrounding them. Other theoretical developments are due to Dijkstra and Wert (1950) who concluded that the coercive force of iron is determined by the volume fraction and state of dispersion of inclusions, its magnitude being largest if their size is of the order of the wall thickness. Kersten (1956) considered the effects of dislocation densities on the coercive force, the domain walls being envisaged as fixed at dislocation centres and as being initially distorted by the applied magnetic fields. Goodenough (1954) treated the effects of granular inclusions, grain boundaries, lamellar precipitates and the crystalline surface on the nucleation of domains of reverse magnetization and on the coercive force, determined by the demagnetizing action of surface magnetic pole distributions around the imperfections. Related



results had been obtained earlier by Kondorsky (1949). Schwabe (1952) found that, if, for a heterogeneous material, the inclusions are non-spherical and small compared with the wall width, slight eccentricities may cause considerable deviations from the coercive forces due to the disperse fields of spherical inclusions.

These and other theoretical developments of the theory of wall motion are primarily relevant for soft magnetic materials and it will therefore suffice to have given references to some of the more important publications. Fuller reviews have been published by Becker and Döring (1939), Stoner (1950), Weil (1951a), Dijkstra (1954), Brenner (1955), Kersten (1955) and Kittel and Galt (1956).

## 2.2. *Fine Particle Theory; Introductory and Fundamental Papers up to 1948*

The high coercivity of many of the magnetically hard materials to be described are most naturally interpreted in terms of rotational magnetization changes in fine particles. This is not to say that a complete explanation in these terms is possible of all the complex observations. In fact, the fine particle approach on the one hand and the wall motion approach on the other are not distinct and frequently overlap in their ranges of applicability, for example, if the particles are so large as to be multidomain (cf. below), if particles coalesce and domain walls are nucleated at the joints (cf. § 3), or if the distinction, in an alloy, of precipitate and matrix is not complete. Indeed, as pointed out by Stoner (1950), the 'disperse fields' developed for completely isolated magnetic particles are no more than their demagnetizing fields, and it is these which determine their coercive force. This thought leads naturally to the hope that a unified treatment including both aspects will one day be developed on the basis of magnetostatic principles (Brown 1958, 1959a). At present, the fine particle approach has the advantage of relative simplicity and wide applicability to many magnetically hard materials for which there is independent evidence that strongly magnetic particles are, in fact, the main cause of hardness.

The earliest mention of the possible single domain character of small particles seems to have been made by Frenkel and Dorfman (1930); they recognized that domain wall formation is unfavourable on energetic grounds if the particle size is below a critical value which was, however, greatly over-estimated. Becker (1930) developed a treatment of irreversible rotational magnetization processes due to what would now be called uniaxial strain anisotropy, and found that the coercive force goes as  $\lambda\sigma/I_0$ , where  $\sigma$  is the stress. Equivalent results for cubic magnetocrystalline anisotropy were first obtained by Akulov (1933), leading to  $H_c \sim K/I_0$ . Neither of these treatments was applied to the physical situation now known to be relevant, the magnetization changes in small particles. Kondorsky (1940) later introduced in a preliminary way the effects of shape anisotropy by realizing that for elongated bodies the coercivity due to irreversible rotations depends on the difference between the demagnetizing factors in

two principal directions. This idea was applied to magnetically soft materials whose elementary domains were treated as long parallel cylinders. Kondorsky (1942) also took some account of interdomain interactions by using an effective field approach (cf. below). Stoner (1940) based his early ideas on the results of the work of Bradley and Taylor (1938 a, b) on Fe-Ni-Al permanent magnet alloys (cf. § 7). This showed that there is an intimate connection between magnetic hardness and the occurrence of small strongly magnetic precipitate particles. He also pointed out that, for elongated iron and nickel particles, the demagnetizing energy differences along and at right angles to the long axes are greater by large factors than the magnetocrystalline or strain anisotropy energies, in line with more recent ideas. Kittel (1946) published the first estimates of critical sizes for single domain behaviour. The calculations were for rods, cubes and spheres, and were based on comparisons of the demagnetizing energies of single domains with the anisotropy and wall energies of multidomains, leading to a critical size about  $0.01 \mu$  for an iron sphere, and larger values for elongated particles. These estimates are based on the assumption that the critical size is well above the domain wall width which is not the case for spherical iron and nickel particles, although it is so for magnetocrystalline controlled materials such as MnBi (cf. § 3), for which estimates of the critical size are about  $0.4 \mu$  (cf. Kittel and Galt 1956), or Ferroxdure (cf. § 5), about  $1.3 \mu$ . Improved calculations for iron and nickel are reviewed below.

Following the development of metallic powder magnets (cf. § 3) Néel (1947 a, b) gave a brief discussion of the theoretical background. The critical size for spherical iron particles was estimated by assuming the lines of force for a non-uniformly magnetized body to be circular, involving a positive exchange energy. This was estimated from the molecular field coefficient and compared with the demagnetizing energy of a single domain, leading to a critical radius  $0.016 \mu$ , close to Kittel's estimate. Néel extended Akulov's (1933) treatment of the hysteretic properties of cubic materials, and found that the coercive force  $H_c$  of spherical particles whose cube edges are randomly oriented is equal to  $0.64 K/I_0$ , where  $K$  is the anisotropy coefficient, giving 160 oersted for the coercivity of iron. This low value led to the extension of the treatment to include shape anisotropy effects (Néel 1947 b), for which  $H_c$  was shown to be proportional to  $(N_b - N_a)$ , the difference in the two principal demagnetizing factors for prolate spheroids. If the polar axes are randomly oriented Néel obtained

$$H_c = 0.48 (N_b - N_a) I_0.$$

His extensions to cover shape variations and particle interactions are considered below. Néel (1947 c) also applied these ideas in a discussion of the properties of anisotropic permanent magnet alloys (cf. §§ 7, 8), presuming that the precipitated particles grow with preferential elongation in the direction of the orienting field so as to reduce the magnetostatic energy. The measurements of Nesbitt and Williams (1957) on Alnico V (cf. § 7) show, however, that the anisotropy is induced, at least for this material, during nucleation rather than growth (cf. also Kittel, Nesbitt and Shockley 1950).



Already in 1943 Guillaud (1949a) had proposed that his results (Guillaud 1943, cf. §3) on MnBi, for which high coercivities over  $10^4$  oersted were observed, could be explained in terms of uniaxial magnetocrystalline anisotropy, leading to maximum coercivities  $2K/I_0$  as first given by Akulov (1933). Guillaud (1947) extended this discussion and also made brief reference to other possible types of anisotropy.

The whole problem was considered in detail by Stoner and Wohlfarth (1947, 1948), continuing the work referred to by Stoner (1940) and started before the war. The critical size for single domain behaviour was estimated for iron and nickel particles by comparing the demagnetizing energy of a prolate spheroidal single domain with principal demagnetization coefficient  $N_a$  with the exchange energy of the particle when this energy is reduced by allowing the magnetization vector to take up uniform orientations between 0 and  $2\pi$  between one end of the equatorial axis and the other. The exchange energy was estimated from the value of the Curie temperature and the effective number of magnetic carriers. The critical values of  $b$ , the semi-equatorial axis, vary as  $N_a^{-1/2}$ , and are equal to  $0.011$  and  $0.024\mu$  for spherical iron and nickel particles respectively; for elongated particles with dimensional ratio  $a/b=10$  the respective values are  $0.047$  and  $0.098\mu$ . The values are, it is stressed, to be regarded as lower limits. Similar calculations for iron oxide particles were given by Morrish and Yu (1955).

Stoner and Wohlfarth (1948) carried out calculations of the magnetization as a function of a reduced field  $h$  for particles below the critical size. Here  $h$  is defined in different ways according to the governing anisotropy, shape, uniaxial magnetocrystalline or uniaxial strain, by the respective formulae

$$h = H/(N_b - N_a)I_0; \quad h = HI_0/2K; \quad h = HI_0/3\lambda\sigma, \quad . \quad . \quad (2.1)$$

in the usual notation. For fully aligned particles the coercive force corresponds to  $h=1$ . This gives for infinitely long iron particles a coercive force  $H_c = 10^4$  oersted due to shape anisotropy, for spherical cobalt particles  $H_c = 6 \times 10^3$  oersted due to magnetocrystalline anisotropy, and for spherical nickel particles under a uniaxial stress  $200 \text{ kg mm}^{-2}$   $H_c = 4 \times 10^3$  oersted. The various reasons why these values are not expected to be attained in practice and the experimental evidence are considered below. The calculations of the 1948 paper also give results for the magnetization of particles oriented at different angles to the field direction, leading to an interpretation of the anisotropic properties of permanent magnet alloys, for the critical angles and fields at which the rotational magnetization changes become unstable, and for the magnetization of a random particle assembly, leading to the hysteresis curve shown in fig. 2.1.

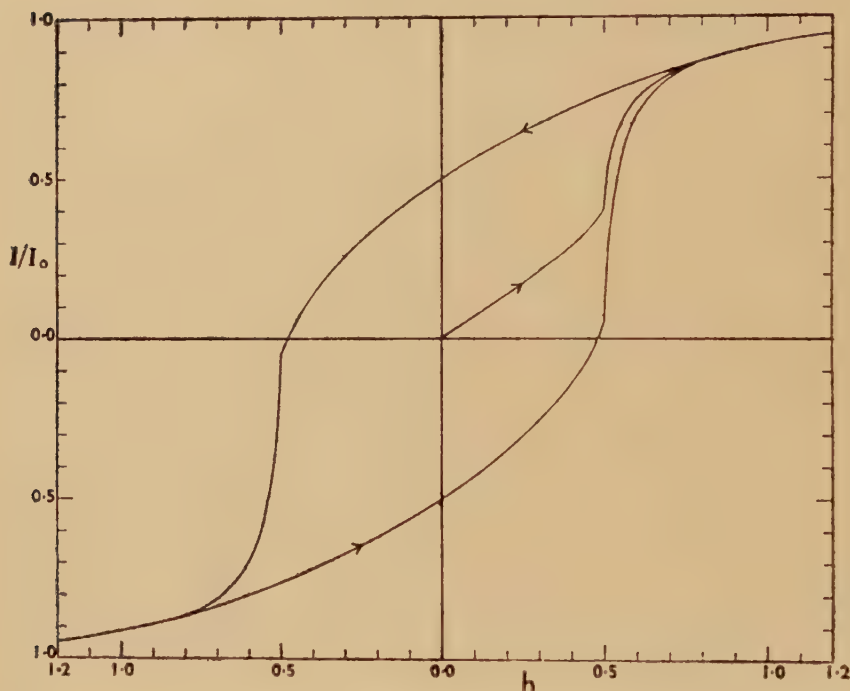
This curve is characterized by a reduced coercivity  $h_c = 0.479$ , reduced remanence  $I_r/I_0 = \frac{1}{2}$  and reduced initial susceptibility equal to  $\frac{2}{3}$ .

### 2.3. Variations of Individual Coercivities in Particle Assemblies

For particles governed by shape anisotropy the coercive force is proportional to the difference of the principal demagnetization coefficients  $(N_b - N_a) = N(m)$ , a function of the axial ratio  $m = a/b$  of the prolate

spheroidal particles. For an assembly  $m$  may vary, and the bulk coercive force is proportional to an appropriate mean of  $N(m)$ . The first calculation of this mean was reported by Néel (1947 b) who assumed that the volume distribution function  $g(m)$  is a constant, but used an inadequate representation of  $N(m)$ . Wohlfarth (1954) considered a variety of forms of  $g(m)$ . These included a Gaussian expression, with applicability to Weil's results for Fe-Ni powders (1948 a, cf. § 3) that  $H_c/I_0$  is approximately constant and equal to about 0.5. This result was obtained by choosing a reasonable value of the mean deviation from spherical shape ( $\bar{m} = 1$ ). For a mixture of particles of which a volume fraction  $c$  has constant coercivity  $H_{c1}$ , less

Fig. 2.1



Hysteresis curve for randomly oriented particles.  $I$ , magnetization;  $I_0$ , saturation magnetization;  $h$ , reduced field defined by relations (2.1). After Stoner and Wohlfarth (1948), Rhodes (1949).

than that of the remainder,  $H_{c2}$ , the bulk coercivity decreases rapidly as  $c$  increases, particularly if  $H_{c1} \ll H_{c2}$ . This result, a particular example of Gerlach's rule (Gerlach 1938), was applied to the results of Meiklejohn (1953, cf. § 3) on mixtures of ex-amalgam iron particles; the agreement was only qualitative. Osmond (1954) used a Gaussian form for  $g(m)$ , a mean  $\bar{m} = 1.3$  and a reasonable mean deviation in calculations of the magnetization curve of  $\gamma$   $\text{Fe}_2\text{O}_3$  powders (cf. § 4). The curve is found to be



smoothed out compared with that shown in fig. 2.1 as a result of the shape variations, and hence the bulk coercivity is lower than that of an assembly of identical particles with  $m = \bar{m}$ .

Bean (1955) considered the bulk coercivity of mixtures of single domain with equal amounts of either small superparamagnetic or large infinitely soft multidomain particles, and found that Gerlach's rule is not always applicable and that the agreement with Meiklejohn's (1953) data is here good. Similar calculations were also reported by Campbell *et al.* (1957) who used a distribution function  $g(m)$  obtained from electron microscope data for Fe and  $\text{Fe}_3\text{O}_4$  mixtures (cf. §§ 3 and 4); they also found, in agreement with Osmond (1954), that the bulk coercive force is below that corresponding to the mean dimensional ratio.

The conclusions to be drawn from these results are that shape variations decrease the coercive forces of particle mixtures to relatively low values. Similar results are also to be expected if the individual coercive forces vary throughout a material as a result of size variations (Bean 1955), non-uniform interactions, variations of the magnetization or of the orientation, domain wall effects in a part of the material, etc., situations which are only too likely to occur in practice, where relatively low coercivities should thus occasion no inordinate surprise.

#### 2.4. Particle Interactions

Except in special substances such as dilute alloys (cf. § 6) the magnetically active particles are usually closely packed and subject to strong interactions which may have a profound effect on the magnetic properties. The first discussion was given by Néel (1947 b) who gave the formula

$$H_c(p) = H_c(0)(1 - p), \quad . \quad . \quad . \quad . \quad . \quad (2.2)$$

where  $p$  is the packing factor, in reasonable agreement with some but not all the experimental data on powders (cf. §§ 3 and 4). This formula was obtained by calculating the magnetostatic interaction energy and relating the coercivity directly to this energy, which is not always justified. Shockley and Kittel (cf. Kittel 1949) considered the particles to be long parallel cylinders in interaction, and calculated the coercivity by lattice summation, a process involving some mathematical uncertainties (conditional convergence difficulties); Néel's formula (2.2) was obtained approximately. Néel (1954 a) used an effective (or 'Lorentz') field approach, considering fluctuations of the amplitude of this field which seem to have an additional effect on the coercive force. Kondorsky (1951) criticized the use of this approach in that it does not allow for short-range effects. To allow for this Kondorsky used an improved formula for the mean susceptibility of an assembly of prolate spheroids and found that

$$\left. \begin{aligned} H_c(p) &= H_c(0)(1 - p/p_0) + C, & p < p_0, \\ H_c(p) &= C, & p > p_0, \end{aligned} \right\} \quad . \quad . \quad . \quad (2.3)$$

where  $p_0^{-1} = (4\pi/3)(2N_a + N_b)/(N_a N_b)$  and  $C$  is a constant. It seems (Wohlfarth 1955 a) that these formulae also are based on a Lorentz field

approach. Kondorsky (1952 a, b) also found that increasing particle interactions influence the critical particle size; if the particles are single domain when isolated they remain so on compression, but if they are multidomain in isolation increasing interactions may cause them to become single domains. This effect has been observed for  $\gamma$   $\text{Fe}_2\text{O}_3$  powders by Morrish and Watt (1957, cf § 4).

Wohlfarth (1955 a) showed that Néel's formula (2.2) may be derived for an assembly of parallel prolate spheroidal particles whose surroundings exert a Lorentz field and thus affect the demagnetization factors which are reduced in the ratio  $(1-p)$ . Further, Néel's method of relating coercivity to magnetostatic energy changes was shown to be unjustified in some cases, for example for spherical particles lying on a lattice. In this paper the method of summation is applied to regularly distributed parallel or non-parallel particles in weak interaction. These cause changes of the effective shape anisotropy coefficients and of the magnetization due to relative rotations of the magnetization vectors in neighbouring non-parallel particles. In general

$$H_c(p) = H_c(0) - ApI_0 - \dots, \quad (2.4)$$

where  $A$  depends on the details of the distribution of the particles and may be of either sign. The differences between the relations (2.2) and (2.3) on the one hand and (2.4) on the other have not yet been explained. If the coercivity of particles is determined by magnetocrystalline anisotropy it should be influenced to a small extent only by their interaction, in agreement with experiment (cf. §§ 3, 4 and 5).

Jacobs and Bean (1955) used a similar method in calculating the coercive force of chains of spheres in strong interaction, and obtained relation (2.4) with  $H_c(0) = 0$  and  $A$  negative. They also found, however, that the coercivity may be reduced if the magnetization vectors reverse incoherently (cf. below). Shtrikman (1957) considered the interaction of infinitely long square cylindrical particles lying on a square lattice and, allowing the magnetization reversals of neighbouring cylinders to be incoherent, obtained a variation of  $H_c$  very close to that given by (2.2) (see also Aharoni 1959).

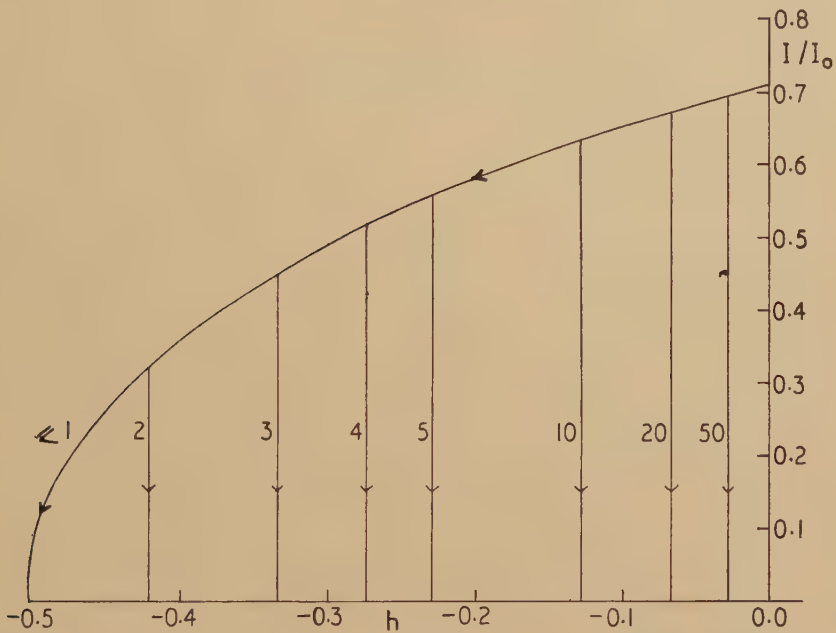
### 2.5. *Non-uniaxial Anisotropy*

If the anisotropy of the particles is uniaxial the mathematical treatment of their magnetic properties is reasonably simple. With non-uniaxial anisotropy the computational difficulties become so great that only a few attempts have yet been made. Néel (1947 a) obtained for randomly oriented iron spheres a coercivity  $H_c = 0.64 K/I_0$ , where  $K$  is the anisotropy coefficient. Stoner and Wohlfarth (1948) extended their treatment of shape anisotropy in prolate spheroids to particles with general ellipsoidal shape. Here the equilibrium position of the magnetization vector is not always one in the plane containing the direction of the applied field and the longest principal axis, and as a result the coercive force may be reduced



to low values. As an example fig. 2.2 shows the demagnetization curves for general ellipsoids with semi-axes  $a, b, c$  ( $a > c > b$ ) and with the field applied in the  $a, b$  plane at  $45^\circ$  to the  $a$ -axis. If the ratio  $(N_b - N_c)/(N_c - N_a)$ , shown on the curves, is less than 1, the full curve for a prolate spheroid is obtained, but if it is above 1 the coercivity is reduced until, when  $a = c > b$ , the particle shape is oblate spheroidal and the coercivity zero.

Fig. 2.2



Demagnetization curves for general ellipsoids.  $I/I_0$ , reduced magnetization;  $h = H/(N_b - N_a)I_0$ ; numbers on curves, ratio  $(N_b - N_c)/(N_c - N_a)$ ;  $H$  applied in  $a, b$  plane at  $45^\circ$  to the  $a$ -axis; semi-axes  $a > c > b$ ; demagnetizing factors  $N_a, N_b, N_c$  such that  $N_b > N_c > N_a$ .

Wohlfarth (1955 b) considered the properties of particles with three equivalent and coplanar easy directions of magnetization, the simplest model of haematite powders (cf. § 4), and calculated the remanence curves. Complete hysteresis curves for haematite powders were obtained by Dzyaloshinsky (1958) who assumed that the number of easy directions in the basal plane is six and treated the case of field direction in this plane. Prache (1957) considered particles with cubic anisotropy and with the field applied in a principal plane, and Ganzhorn (1958) obtained the complete hysteresis curve for random cubic particles using an electronic computer which had to carry out over  $10^6$  operations.

The remanent magnetization of particles with a variety of different types of non-uniaxial anisotropy has been calculated by Wohlfarth and

Tonge (1957) and Tonge and Wohlfarth (1958), who considered regular planar and spatial distributions of equivalent easy directions of magnetization, mixed uniaxial anisotropies and mixed uniaxial + cubic anisotropies. It was found that whenever one uniaxial component is present in any strength compared with other components the remanence of random particles quickly approaches  $\frac{1}{2}I_0$ . The last-mentioned problem is particularly important in a number of applications, for example for slightly elongated iron or iron oxide particles or for cubic materials such as cobalt ferrite (cf. § 5) for which uniaxial anisotropy may be induced by magnetic annealing.

Another practical problem is concerned with the elongated iron particles of Paine *et al.* (1955, cf. § 3) whose frequently observed dendritic outgrowths make the anisotropy definitely non-uniaxial.

## 2.6. *Some Miscellaneous Results*

Brown and Morrish (1957) investigated the effect on the coercive force of the presence of a non-magnetic cavity inside a single domain particle, with particular reference to  $\gamma\text{Fe}_2\text{O}_3$  powders (Osmond 1952, 1953, Morrish and Yu 1955, Campbell 1957, cf. § 4). It was shown that for a hard spheroidal particle the cavity causes a reduction of the coercive force. Brown and Morrish also derived a general result for particles of arbitrary shape, that it is in principle possible to treat them as general ellipsoidal with effective principal demagnetization coefficients, as long as the magnetization is uniform. This theorem should find considerable use in future calculations, and has already been applied by Shtrikman (1957) to the interaction problem.

Néel (1953 a, 1954 b) showed that the dipolar interaction forces between the magnetic carriers of a small particle not only lead to magnetostrictive effects (Becker 1930) but also to anisotropy effects due to the asymmetry introduced by the surface of the particle. This 'surface anisotropy' becomes important compared with the shape anisotropy of prolate spheroidal particles with semi-minor axis about  $0.008 \mu$ . The effect has not been observed, presumably since for such small particles the thermal fluctuation effects, to be discussed now, become important.

## 2.7. *Thermal Fluctuations in Small Particles*

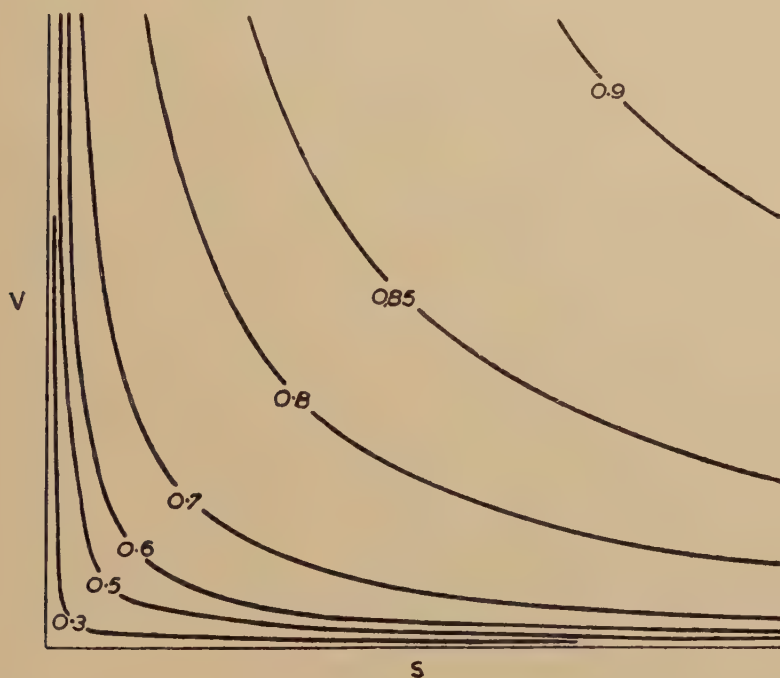
In the theoretical work discussed so far it was assumed that the magnetization of a particle remains stable except during irreversible rotations in an applied magnetic field. Néel (1949 b) showed that at finite temperatures the magnetization of a sufficiently small particle may reverse spontaneously even in the absence of a field, due to the effect of thermal and mechanical forces in overcoming the energy barrier between two otherwise easy directions of magnetization. The process is characterized by a relaxation time  $\tau$ , where

$$\tau^{-1} = f_0 \exp(-vH_c I_0 / 2kT), \quad . \quad . \quad . \quad . \quad . \quad (2.5)$$



$f_0$  being a slowly varying frequency term of order  $10^9$  c/s and  $v$  the particle volume. For iron particles  $\tau$  was found to vary from  $10^{-1}$  to  $10^9$  sec as  $v/T$  changes from  $3.2 \times 10^{-21}$  to only  $7.0 \times 10^{-21}$  cm<sup>3</sup> deg<sup>-1</sup>. Hence outside a relatively narrow range of particle volumes the magnetization is either completely stable and full ferromagnetism is developed as already discussed, or completely unstable with development of superparamagnetism (cf. § 6). At room temperature the dividing region is close to the volume of a spherical iron particle of radius  $0.008 \mu$ . Néel extended the discussion to the effects of a magnetic field applied parallel to the

Fig. 2.3



Thermal fluctuations in small particles.  $v$ , particle volume;  $s$ , shape anisotropy coefficient; numbers on curves, ratio of  $T$  to the Curie temperature; schematic. After Néel (1949 b).

polar axis, and of variations in a particle assembly of the individual relaxation times. These may occur as a result of shape and size variations, and fig. 2.3 shows a family of curves relating particle volume  $v$  with the shape anisotropy coefficient, each curve being characterized by the ratio of  $T$  to the Curie temperature. For all particles in an assembly which are represented by points to the left of a given curve the magnetization is unstable and obeys a Langevin law; points to the right of the curve characterize stable particles. The curves are distorted by the application of a magnetic field, and the resulting analysis has been used widely in

discussing the problems of rock magnetism (cf. Néel 1955 a). For a mixture of stable and unstable particles the bulk coercivity is expected to decrease rapidly below its maximum value as has been observed (cf. §§ 3, 4). For any particular material the importance of this effect can always be assessed by carrying out measurements at different temperatures (Weil 1949 b, § 3). Further discussion of superparamagnetism is given in § 6, and a comprehensive review by Bean and Livingston (1959).

### 2.8. *Size Dependence of Coercive Force; Multidomain Particles*

As shown by the measurements discussed in §§ 3, 4 and 5 the coercive force of particle mixtures decreases as the particle size increases beyond the range where thermal fluctuations are effective. This decrease is ascribable to the formation of domain walls and is observed to be approximately inversely proportional to the particle size. The theoretical treatment of the coercive force of multidomain particles is very difficult, and only preliminary results have so far been obtained. The first discussion is due to Kittel (1948), who considered the balance of the energy of formation of the domain wall, the energy of the wall in the external field  $H_c$  and the change of the self energy of the spherical particle in which the wall is formed. The rough agreement of Kittel's result with Guillaud's (1943, 1949 b) data on MnBi (cf. § 3) is, however, fortuitous, as a corrected estimate of the self energy term in this treatment gives the coercive force independent of particle size (Rathenau *et al.* 1952, Néel 1956), in disagreement with observation (but see Ohoyama (1957) who in turn corrected the calculation by the addition of a further size dependent term which becomes significant if the size is relatively small; other early attempts at interpreting the observed size dependence are due to Guillaud (1949 b) and Dijkstra (1954)). Néel (1956) considered a cubic particle containing a number of internal and closure domain walls. The energy to be minimized contains contributions from the magnetocrystalline energy of the closure domains, the exchange energy of the principal internal domain walls and, a new term, the magnetostatic energy arising from the presence of free magnetic poles associated with these walls. The coercive force calculated for this model varies as  $d^{-2/3}$ , where  $d$  is the linear dimension of the cubic particle, but the quantitative agreement with observation is poor, especially for MnBi where the calculated and measured values differ by a factor about 10. Néel ascribed this disagreement to the neglect of the wall nucleation energy, about which little is known. Behringer and Kittel (cf. Kittel and Galt 1956) find that the size dependence of the coercive force of spherical multidomain particles can only be accounted for by the presence of nuclei of reverse magnetization formed at equatorially placed imperfections.

Amar (1957, 1958 a) extended Néel's (1956) calculation by further consideration of his magnetostatic energy term. A 2-domain cube of iron was treated, and the energy calculated on the basis of formulae given by Rhodes and Rowlands (1954). The wall thickness and energy were



found to differ markedly from their values in a bulk material; the thickness increases and the energy decreases on raising the particle size. Amar found that the 2-domain configuration becomes unstable when the cube edge has a length less than about  $0.02 \mu$ , in agreement with other critical size estimates. This work is a first step of a full treatment of multidomain particles. Such a treatment will have to include consideration of nucleation effects as already pointed out. In order to calculate the magnetization of a multidomain in an external field, and, in particular, the coercive force, it is also necessary to consider how the propagation of the wall, once nucleated, can take place. For magnetocrystalline controlled particles such as MnBi (cf. § 3) the domain wall is narrow compared with the critical size and a large volume fraction of the particle is thus uniformly magnetized. Hence the problem of wall motion should not be insuperable. For iron and nickel particles of size not too far above critical the whole material is, however, in a state of non-uniform magnetization, and here the magnetization process, intermediate between rotation and wall motion, seems difficult to envisage.

An alternative approach to this problem is based on a consideration of the variation of the magnetization throughout a magnetic particle, as described below.

### 2.9. Incoherent Rotations

It has so far been assumed that in the absence of thermal effects the magnetization of a single domain particle is, as this name implies, uniform under all conditions, both in the absence of a field and during reversible and irreversible magnetization changes. It may, however, happen that the irreversible magnetization changes can take place incoherently and in lower fields than the corresponding coherent changes, leading to a decrease of the coercive force compared to the previous estimates.

This result was obtained by Jacobs and Bean (1955) for particles in the form of chains of uniformly magnetized spheres which were taken to be coalescent though without wall nucleation. When a magnetic field applied parallel to the chain direction is reversed, the eventual rotations of the magnetization vectors take place in opposite directions in alternating spheres ('fanning') and in lower fields than would be required for parallel rotations, so that the latter never take place and the coercive force is reduced. As the angle  $\theta$  between the directions of the chain and field increases this tendency towards incoherent reversals decreases and the coercive force increases. Finally, at angles  $\theta$  above about  $70^\circ$  the reversals are always coherent. The variation of coercive force  $H_c$  with  $\theta$  thus passes through a maximum which has in fact been observed for Fe and Fe-Co powders (Luborsky *et al.* 1957, Jacobs and Luborsky 1957). The calculations of Jacobs and Bean were directed towards an interpretation of the relatively 'low' coercive forces of the elongated metal powders produced by Paine *et al.* (1955, cf. § 3). They may be criticized on several grounds (e.g. the model is not likely to be generally applicable in all its

details, the magnetization of each sphere is likely to be severely non-uniform due to the presence of close neighbours, and slight elongations of the spheres at an angle to the chain direction could suppress the incoherent rotations); their chief value lies in the realization that there are physically plausible conditions under which incoherent magnetization changes can take place.

This problem was taken up in its most general form by Brown (1957), following on earlier magnetostatic investigations. He considered the change in free energy between a given state of uniform magnetization of a particle under the influence of a reverse field, and neighbouring states of uniform and non-uniform magnetization. The instability of the initial state is determined by the solution of a complicated boundary value problem, whose eigenvalues determine whether the magnetization reversals in the field take place coherently or incoherently. The problem was partially solved for a prolate spheroid with the field parallel to the polar axis  $a$ , and it was found that if the semi-equatorial axis  $b$  is less than  $b_c$  the reversals are coherent, and vice versa, where

$$b_c = (\alpha/I_0)(C/N_b)^{1/2}, \quad . \quad . \quad . \quad . \quad . \quad (2.6)$$

and where  $\alpha$  is a constant of order 2 and  $C$  the usual exchange or stiffness constant (cf. Kittel and Galt 1956). Also if, for spheres,

$$\text{and if } \left. \begin{array}{ll} b < b_c, & H_c = H_c(0), \\ b > b_c, & H_c \geq H_c(0) - \frac{4}{3}\pi I_0(1 - b_c^2/b^2), \end{array} \right\} \quad . \quad . \quad . \quad (2.7)$$

where  $H_c(0)$  is the coercive force due to coherent rotations. Relation (2.7) gives the size dependence of coercive force sought in § 2.8, but does not seem to have been compared with experiment. Relation (2.6) for  $b_c$  differs from that for the critical size calculated by Stoner and Wohlfarth (1948),  $b_c'$  say (this being the size above which the magnetization is non-uniform *even in the absence of a field*), which involves  $N_a$  rather than  $N_b$  and has  $\alpha = \pi$ , so that  $b_c/b_c' \simeq \frac{2}{3}$  for spheres and  $b_c/b_c' \rightarrow 0$  for long cylinders.

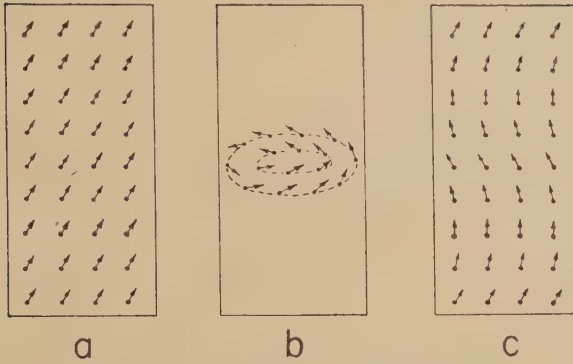
The same problem had been considered earlier by Kondorsky (1952 a, b) who used the more manageable Ritz variational method involving two parameters and derived relations equivalent to (2.6) and (2.7). Frei *et al.* (1957) considered three modes of magnetization reversals for an infinite cylindrical particle; these are illustrated in fig. 2.4, where (a) depicts coherent rotations and (b) and (c) respectively rotations by 'curling' and 'buckling'. The results of a variational calculation for an infinite cylinder parallel to the field are shown in fig. 2.5, where effectively the reduced coercive force  $H_c/2\pi I_0$  is plotted as a function of the reduced radius  $S = R/R_0$ , where  $R_0 = C^{1/2}/I_0$ , for the three modes illustrated in fig. 2.4. The lowest  $H_c$  is the one which is physically significant. For  $R/R_0 \gtrsim 1.1$  the mode of reversal is that of curling for which

$$H_c = \beta C/I_0 R^2, \quad . \quad . \quad . \quad . \quad . \quad (2.8)$$

where  $\beta = 6.78$ , to be compared with (2.7); for  $R/R_0 \gtrsim 1$  the coercive force reaches its maximum value corresponding to coherent rotations,  $H_c(0) = 2\pi I_0$ . The critical value  $b_c$  separating effectively coherent and

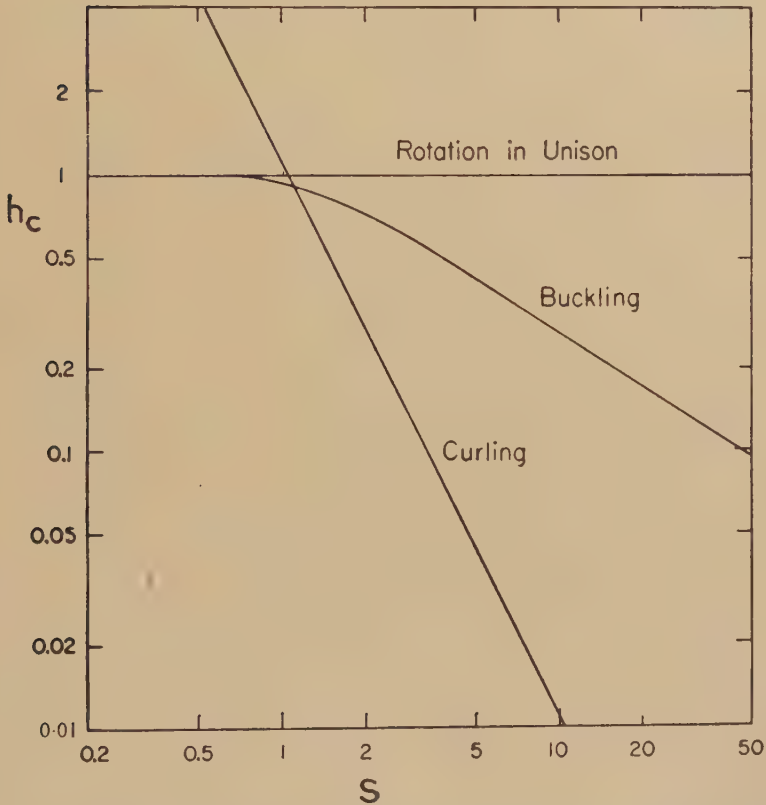


Fig. 2.4



Modes of magnetization change for an infinite cylinder. (a) coherent; (b) curling; (c) buckling; schematic. After Frei *et al.* (1957).

Fig. 2.5



Reduced coercive force for infinite cylinder.  $h_c = H_c / 2\pi I_0$ ;  $S = R/R_0$ , where  $R$  is the cylinder radius; modes illustrated in fig. 2.4. After Frei *et al.* (1957).

incoherent rotations was also estimated for a prolate spheroid and was found to be given by (2.6) with a rather different  $\alpha$ . Aharoni and Shtrikman (1958) repeated the cylinder calculations by solving completely Brown's (1957) boundary value problem. The results are closely similar to those shown in fig. 2.5. It was also pointed out that in no case do the magnetization reversals for infinite cylinders take place coherently. This may be so, but, as seen in fig. 2.5, the coercive force at least approaches its maximum coherent rotation value  $2\pi I_0$  for a small cylinder radius and, since elsewhere the magnetization is uniform, the distinction implied by this statement seems to have little physical significance in this connection.

It remains to be seen what results are obtained for other and more realistic particle shapes. The required calculations of the solutions of Brown's equations are impracticable except by using powerful electronic computers, and such work is at present being undertaken by Brown and by the Rehovoth group. Brown (1958, 1959 a) has pointed out that physically significant calculations should include consideration of specimen finiteness and imperfections. For a cylindrical particle the calculations described (see also Shtrikman and Treves 1959) only lead to non-uniform states of magnetization during unstable incoherent rotations, the magnetization being otherwise uniform. The extensions envisaged by Brown may lead to stable non-uniform states even for a cylinder (Brown 1958), and, when applied more widely, may eventually give valuable information about the nucleation of magnetization reversals not only in small particles but also more generally in bulk materials. Brown (1959 a) in fact hopes that 'micromagnetics' could eventually replace domain theory (see also Brown 1959 b, Aharoni 1959).

### 2.10 *Further Applications*

The results of the theoretical work described above have been applied to a number of problems.

The remanent magnetization after saturation  $I_r$  may be calculated fairly easily; Gans (1932) obtained effectively  $I_r/I_0 = 0.5, 0.831, 0.866$  for randomly oriented uniaxial, + and  $-K$  cubic particles respectively. Results for more complicated distributions of easy directions of magnetization were obtained by Wohlfarth and Tonge (1957) and Tonge and Wohlfarth (1958). The effect of particle interactions on the remanence is more difficult to assess; for one example Wohlfarth (1955 a) found a slight increase of  $I_r/I_0$  accompanied by a slight decrease of coercivity. Shape variations influence the bulk coercivity of a prolate spheroidal particle mixture but leave  $I_r/I_0 = \frac{1}{2}$  if the particles are randomly oriented (Wohlfarth 1954). If the particles are partially aligned, as in practice after magnetic orientation, the remanent magnetization has values depending on the precise mode of disalignment, as has the variation of remanence with angle relative to the preferred direction of the anisotropic mixture. For example (Wohlfarth 1959), if the particles are uniaxial with the easy axes all oriented at an angle  $\theta_0$  to the preferred direction ('conical model') then, with  $j_r = I_r/I_0$ ,

$$j_r^{\parallel} = \cos \theta_0, \quad j_r^{\perp} = (2/\pi) \sin \theta_0, \quad . \quad . \quad . \quad . \quad . \quad (2.9)$$



with easily calculable intermediate values. For a mixture of random single domain and superparamagnetic particles the deviations of  $j_r$  from  $\frac{1}{2}$  may be used (Weil 1957, cf. § 6) to estimate the relative volume fractions. For particles undergoing incoherent rather than coherent magnetization reversals  $j_r$  is evidently unaffected, but for multidomain particles the reduced remanence decreases as in bulk materials.

Of greater interest are the curves relating the reduced remanence  $j_r = j_r(H)$  with the strength of a previously applied field  $H$ . For uniaxial single domain particles with random orientation (Wohlfarth 1955 c)

$$j_r(h) = 0 \quad (h < \frac{1}{2}), \quad j_r(h) = \frac{1}{2} \quad (h > 1), \quad . \quad . \quad . \quad (2.10)$$

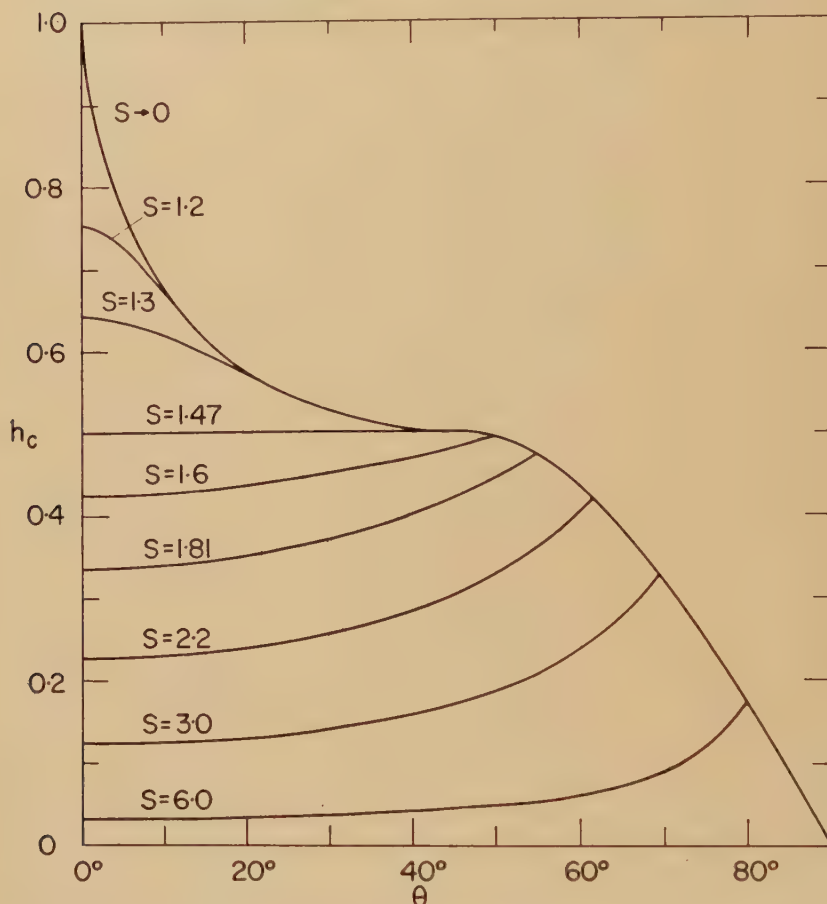
where  $h$  is the reduced field defined by (2.1). The remanence curves are thus smoothed out as a result of shape variations or other changes of the individual particle coercivities, which can in principle be analyzed in this way (Johnson and Brown 1958 a, b, 1959 a). Remanence curves are important in the applications of magnetic recording tapes (cf. § 4). Wohlfarth (1958, cf. also Kondorsky 1940) has shown that there are simple relations between  $j_r(H)$  curves and curves obtained after d.c. or a.c. demagnetization of the remanence. These relations hold whatever the degree of alignment and the variation of the uniaxial anisotropy of non-interacting single domains, but a first test for iron oxide powders (Johnson and Brown 1958 b) shows them not to hold very well, for several imaginable reasons. Other modes of influencing the remanence (Starceva and Shur 1956, Valenta 1959) may also be related to  $j_r(H)$  curves (Wohlfarth 1958, unpublished). Other work on remanence curves includes that of Wohlfarth (1955 b) on particles with non-uniaxial anisotropy, Néel (1949 b) on the influence of thermal fluctuations and Shtrikman (1958) on that of incoherent rotations (see also Aharoni 1959).

The initial susceptibility of single domain particles has also been given, in effect, by Gans (1932). Aharoni *et al.* (1957) calculated the complete reversible susceptibility tensor. As Néel (1954 a, 1955 a) points out, the Rayleigh law is not obeyed for a mixture of identical single domain particles in weak fields, and he suggested that this difficulty may not arise if interactions or multidomain effects are taken into account. Rhodes and Wohlfarth (1954, unpublished) showed that particle shape variations may have similar effects. Wohlfarth (1957) calculated the anhysteretic and anhysteretic remanence curves for a simple distribution of partially aligned particles, and obtained reasonable agreement with Gould and McCaig's (1954) measurements on Alcomax III (cf. § 7). The decrease of the anhysteretic remanence if the exciting fields are too small is analogous to the drop of  $I_r(H)$  curves discussed above (cf. relation (2.10)), but this analogy has not yet been tested.

The coercive force of single domain particles has already been discussed. Among extensions of interest are those of Shtrikman and Treves (1959), who calculated the variation of  $H_c$  with the angle relative to the axis of an infinite cylinder whose magnetization may reverse incoherently.

The results are shown in fig. 2.6; for large reduced size  $S$  (equal to the ratio of the cylinder radius  $R$  to the characteristic length  $R_0 = C^{1/2}/I_0$ ), the angular variation shows a maximum similar to that occurring for the chain of spheres model (Jacobs and Bean 1955, Jacobs and Luborsky 1957). For a mixture of partially aligned particles the angular variation of  $H_c$  may be

Fig. 2.6



Angular variation of coercive force for an infinite cylinder.  $h_c = H_c/2\pi I_0$ ;  $\theta$ , angle between field and cylinder axis;  $S$ , reduced cylinder radius. After Shtrikman and Treves (1959).

quite complicated. Jacobs and Luborsky find that for chains of spheres of which a fraction only is aligned parallel to the preferred direction the coercivity maximum is smoothed out, and the perpendicular coercivity  $H_c^\perp$  increases quite rapidly as the aligned fraction decreases. Wohlfarth (1959) considered a variety of other modes of disalignment in partially aligned particle assemblies. For the 'conical model' discussed above the angular variation exhibits a slight maximum for not too small values of the



semi-vertical angle  $\theta_0$ . Also, for this model, the remanence coercivity  $H_R$  (the d.c. field required to reduce to zero the remanence after saturation) is larger perpendicular to the preferred orientation than parallel to it:  $H_R^\perp/H_R^\parallel = 1.035 \pm 0.005$  over a wide range of  $\theta_0$ . Values of this ratio lying above 1 have often been observed, for example by Becker (1958) for magnetically annealed Cu-Co alloys (cf. § 6). For a simple 2-dimensional mode of partial alignment it is even possible, using the infinite cylinder model with incoherent rotations, for  $H_c^\perp/H_c^\parallel$  to lie above 1 as long as  $S$  and  $\theta_0$  are not too small. Here  $H_R^\perp/H_R^\parallel$  is even more likely to lie above 1, as Becker observed. This ratio also seems to be strongly affected by superparamagnetic effects.

Bean and Meiklejohn (1956) calculated the rotational hysteresis  $W_r(H)$  (the energy change produced by rotating completely a magnetic field of strength  $H$  across a magnetic specimen) for uniaxial single domain particles. The contributions to  $W_r$  come from the irreversible magnetization changes which only occur over the range of reduced fields  $\frac{1}{2} \leq h < 1$  (cf. fig. 6.2). Hence measurements of  $W_r(H)$  allow the spectrum of critical fields of particle mixtures to be investigated (cf. Berkowitz and Flanders 1957, Jacobs and Luborsky 1957, Campbell *et al.* 1957, §§ 3, 4, 6). The integral

$$R = \int_0^\infty \left( \frac{W_r}{I_0} \right) d \left( \frac{1}{H} \right), \quad . . . . . (2.11)$$

which is independent of anisotropy variations, has a value about 0.4 if the irreversible magnetization changes are coherent. For chains of spheres (Jacobs and Luborsky 1957) and infinite cylinders (Shtrikman and Treves 1959) incoherent rotations may increase this value of  $R$  by factors up to 10, and measurements of  $R$  for various materials give, in fact, values larger by factors about 2 or 3. This finding has frequently been canvassed with enthusiasm as a major piece of evidence in support of incoherent rotation models.

Energy effects for single domain particle assemblies had been considered previously by Rhodes (1949), who calculated the thermal changes accompanying irreversible magnetization changes along the hysteresis curve.

### § 3. METALLIC POWDER MATERIALS

The magnetic hardness of fine metallic powders provides perhaps the most direct evidence for the concept of rotational processes in single domains. The properties of the magnets produced from powders are in many cases so excellent that their commercial development offers many attractions. For both these reasons a vast amount of experimental work has been carried out on metallic powder materials, and this is reviewed below.

#### 3.1. Iron, Cobalt, Nickel and their Alloys; Early Developments, mainly in France

Early experiments on fine iron powders (Nagaoka, Antik and Kubyschkina, Honda), suggesting magnetic hardness, culminated in the development of a magnet material by Dean and Davis (1941) and particularly by Néel and

associates (Société d'Ugine 1947 a, b). Dean and Davis electrodeposited iron, cobalt and other metals and alloys into a mercury cathode and removed the mercury by filtration, magnetic separation or centrifugal action, followed by distillation. Small amounts of non-magnetic additives, such as zinc, aluminium or chromium, were stated to inhibit particle growth and to reduce pyrophoric behaviour. After compression permanent magnets were produced with coercivity up to 600 oersted and remanent induction up to  $1.1 \times 10^4$  gauss.

The method used by Société d'Ugine is entirely different. It consists of the decomposition of certain salts of iron, cobalt or their alloys (formates, oxalates, hydroxides, carbonates) at low temperatures (300–400°C) in a reducing atmosphere of hydrogen delivered at a controlled rate. The pyrophoric metal powder is embedded in a protective medium (acetone, ether, benzene) and may then be compressed to any desired density, if necessary in the presence of a non-metallic binder; the density determines to a large extent the magnetic properties of the final product (see below). The first patent specification (Société d'Ugine 1947 a) quoted coercive force values up to about 500 oersted for iron and 1400 oersted for Fe–Co, and remanent inductions up to  $6 \times 10^3$  gauss. The second one (Société d'Ugine 1947 b) describes the effects of adding salts of Ca, Mg, Al or Cd into the original iron or iron–cobalt salts, the metal powders containing about 1% CaO, etc. These additional were stated to increase the remanence and coercivity (from 400 to 550 oersted in one example), and probably act as dispersion agents or by inhibiting particle growth. A fuller discussion of the preparation and properties of the French powder magnets was given at the time by Steinitz (1948), and the properties of the commercial magnets, produced in England under licence, have been described by Polgreen (1954, 1955).

Simultaneous with these commercial developments, and, in fact, helping to make them possible, Néel developed the theoretical ideas described in § 2, and Weil and his associates carried out fuller experimental investigations.

The first important question was the pressure dependence of the coercive force which was given by Néel (1947 b) as following relation (2.2). This relation was verified by Weil (1947) for Fe and Fe–Co powders ( $0.1 < p < 0.5$ ,  $p$  being the packing factor) and by Weil (1948 a) for Fe–Ni with iron contents between 10% and 50% and  $0.2 < p < 0.5$ . For the Fe–Ni powders Weil also verified the linear dependence of  $H_c(0)$  on the saturation magnetization  $I_0$  (cf. § 2). For pure nickel powders, however (Weil 1951 a), Néel's relation between  $H_c$  and  $p$  was not verified for  $p$  between 0.1 and 0.4 where  $H_c$  is practically constant, and it was only for higher values of  $p$ , between 0.4 and 0.6, that a decrease of the coercive force was observed. Similarly, for pure cobalt powders  $H_c$  was found to remain constant over the range  $0.2 < p < 0.6$  (Weil 1951 a), due to the governing magneto-crystalline anisotropy. The compression dependence was also investigated by Lihl (1950) for iron powders with  $0.3 < p < 0.5$ , giving a linear dependence, by Carman (1955 b) for iron powders with particles of varying size and by

Luborsky (1957) for iron dispersed in mercury and with  $H_c(0) = 965$  oersted and  $0.01 < p < 0.1$ , over which narrow range Néel's relation is obeyed.

Weil also measured the temperature variation of the coercive force. Weil and Marfoure (1947) reported results for partially sintered nickel powders, and found a maximum coercivity 200 oersted at  $90^\circ\text{K}$ . Later measurements by Weil (1949 a) extended the temperature range down to  $20^\circ\text{K}$ ; the ratio  $H_c(20^\circ)/H_c(90^\circ)$  was found to equal the ratio of the anisotropy fields  $K/I_0$  at these two temperatures, which would imply that magnetocrystalline rather than shape effects are predominant in nickel powders. However, at  $350^\circ\text{K}$ , where  $K/I_0$  is very small, the coercivity still retains a value about 80 oersted.

For cobalt powders prepared with different proportions of the cubic and hexagonal phases, Weil *et al.* (1948) observed minima in the coercivity, temperature curves close to but somewhat below the isotropy point ( $530^\circ\text{K}$ ). Even at the minima, which are most pronounced if the proportion of the cubic phase is small, the coercivity still has an appreciable value (100–200 oersted), pointing again to mixed shape and magnetocrystalline anisotropy effects. A further complication arises from the unknown polycrystalline nature of the cobalt particles which may, according to McCartney and Anderson (1947), be formed as large hexagonal platelets each containing many individual particles. Weil (1951 a) also attributed compression independence of the coercive force of cobalt powders to this effect of agglomeration, the effect of pressure on the interparticle cavities being thought to be unimportant. It is, however, more likely that the independence arises from the fact that for hexagonal cobalt powders the governing anisotropy is magnetocrystalline (cf. § 2).

The temperature variation of coercivity has also been investigated by Galt (1950) for an alloy containing 68% Ni, 32% Fe whose magnetocrystalline anisotropy coefficient is zero over the temperature range investigated. Here  $H_c$  was found to vary more strongly with temperature than would be implied by a simple effective shape or strain anisotropy. Galt ascribed this result to the size of his particles which, ranging up to  $0.3\ \mu$ , is for the majority of the particles beyond the critical size, and also to a possible polycrystallinity of the particles.

Many of these earlier experimental results on metal powders indicated that it is only in some cases that the particles investigated had sizes in the single domain range. The effects which are observed when thermal fluctuations in very small particles become important and tend to suppress ferromagnetism are discussed in §§ 2 and 6. In other cases the particles may be too large for single domain behaviour and the magnetic hardness is again reduced, as discussed in § 2. Apart from a reduction due to the formation of domain boundaries in the particles it may also happen that the particles themselves are small but coalesce into larger clusters or clumps containing many cavities, as observed, for example, by McCartney and Anderson (1947). Clustering may be due to the attractive magnetic forces between the individual particles, to surface tension or related

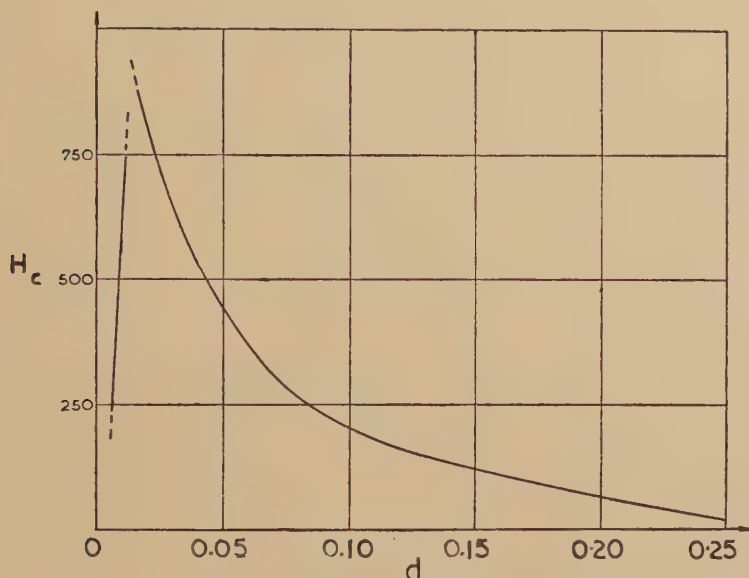


effects, and is particularly strong after partial sintering. Weil (1950) imagined the contact regions between the particles in a cluster to be well defined and to form 'ferromagnetic bridges' which separate non-magnetic cavities. Domain boundaries may be nucleated on these bridges, and their movement determines in part the bulk coercivity of the material. If the bridges are wide this movement is relatively easy, leading to low coercivity. Even if the boundary movement requires fields above the coercive forces arising from rotational processes in the individual particles at low temperatures, fluctuation effects may become important at higher temperatures, increasing the ease of boundary movement and lowering the coercivity. According to Weil (1950) this effect may be responsible for Galt's (1950) anomalous results for Fe-Ni powders, and also for the observed compression dependence of the coercivity of such powders before and after partial sintering and investigated at low and at high temperatures (Weil 1951 b, 1953). The effect of cluster formation has also been discussed by Kopelman (1952) who finds from electron microscope studies that iron particles tend to form 'doughnut' shaped clusters, thus reducing the magnetostatic energy. This effect arises even more strongly for elongated ferromagnetic particles, discussed below.

Domain boundary formation, either in the particles themselves or at regions of contact between particles in a cluster, thus affects their coercive force, and several measurements of the size dependence of coercivity were reported. Weil (1948 b) measured the size of iron powders by determining the heat of wetting with organic liquids and comparing the results with those for larger carbonyl iron particles of known size. Assuming the particles to be spherical the mean diameter was found to be about  $0.045 \mu$ ; this value was somewhat above the diameter obtained from x-ray observations, due, perhaps, to partial sintering (see below). These x-ray line width measurements were carried out by Bertaut (1949, 1953), and fig. 3.1 shows his measured variation of the coercivity of iron as a function of particle diameter which could be controlled by varying the reduction temperature (here from about  $250^\circ\text{C}$  for the smallest to about  $650^\circ\text{C}$  for the largest particles, the temperature for optimum coercivity being about  $300^\circ\text{C}$ ). The maximum  $H_c$  approaches 1000 oersted for a particle diameter about  $0.02 \mu$ , close to the calculated critical value for iron (cf. § 2). The decrease for smaller particles must be ascribed to fluctuation and for larger ones to multidomain effects. Similar results were also obtained in other investigations. Weil (1949 b) measured the coercivity of very fine ( $0.005 \mu$ ) catalytic nickel powders at room temperature, where the coercivity was only 10 oersted, and at  $20^\circ\text{K}$ , where it had risen to 162 oersted due to the suppression of thermal fluctuations (cf. also §§ 2 and 6). Mayer and Vogt (1952) followed the growth of ex-amalgam iron during ageing, and observed a decrease of coercivity as the particle size increases (cf. also § 6). This work has been extended by Luborsky (1957). Meiklejohn (1953) prepared iron and cobalt particles of varying size by electrodeposition in mercury; the deposits were heated

at 200°C for varying lengths of time and were removed from the mercury by the diffusion of oxygen which forms an oxide layer on the surfaces of the particles and allows them to be collected. The particle sizes were measured by electron microscopy and ranged from about  $0.01\mu$  to  $0.5\mu$ . Meiklejohn's results, shown in fig. 3.2, are similar to those of Bertaut (1949, 1953). Similar results have also been reported by Torkar *et al.* (1958) on carbonyl iron. Kandaurova (1957) reported coercivity measurements on Co and Co-Cr powders of size ranging up to  $1200\mu$  and obtained a complicated variation.

Fig. 3.1



Size dependence of the coercivity of iron powders.  $H_c$ , coercive force;  $d$ , particle diameter in microns. After Bertaut (1953).

An experiment demonstrating the essential single domain character of  $0.02\mu$  nickel particles and the multidomain character of  $8\mu$  particles was reported by Kittel *et al.* (1950). For the smaller particles the field required for magnetic saturation was 550 oersted, of the order of the coercive force, but for the larger ones this field was larger, about 2100 oersted, since here the large demagnetization energy of the multidomain structure must be supplied by the external field (cf. also Kittel and Galt 1956).

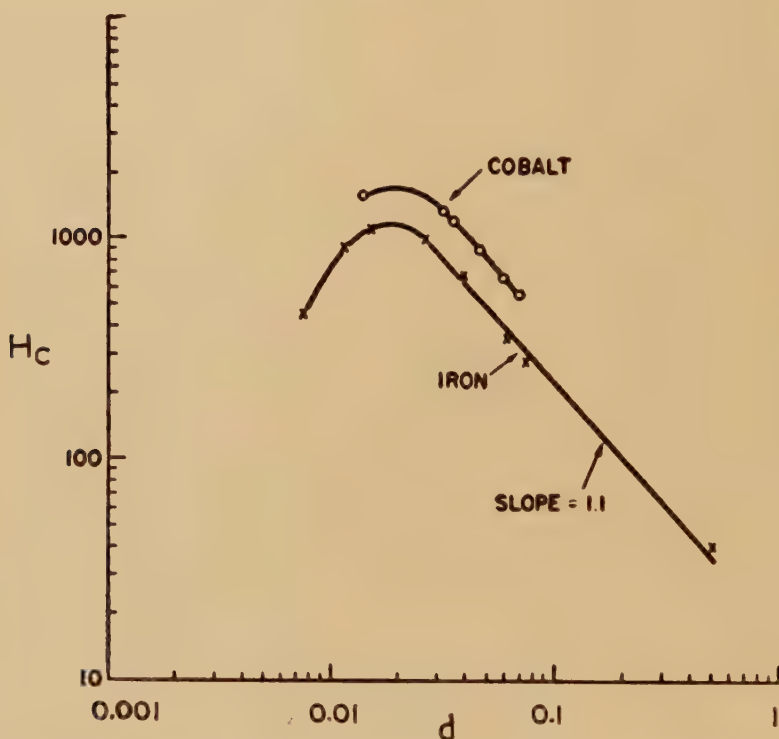
### 3.2. Later Developments

After the scientific and industrial importance of the French investigations had been fully recognized, other and similar investigations were started in a number of places.

Pawlek (1950) gave one of the earlier descriptions of the preparation of ex-amalgam powder compacts of iron and cobalt, and investigated the

temperature variation of the coercive force. For a cobalt powder a coercive force 675 oersted and a maximum energy product  $1.24 \times 10^6$  gauss-oersted was observed at  $83^\circ\text{K}$ . Lihl (1950) prepared iron powders by the low-temperature reduction of the formate, and measured the reduction time (2–4 hours), dependent on temperature, required to produce a relatively oxide free material. Further reduction causes a drop of coercive force due to particle growth and sintering. Similar results were also obtained for Fe–Co powders, further investigated by Lihl in 1953. As cobalt

Fig. 3.2



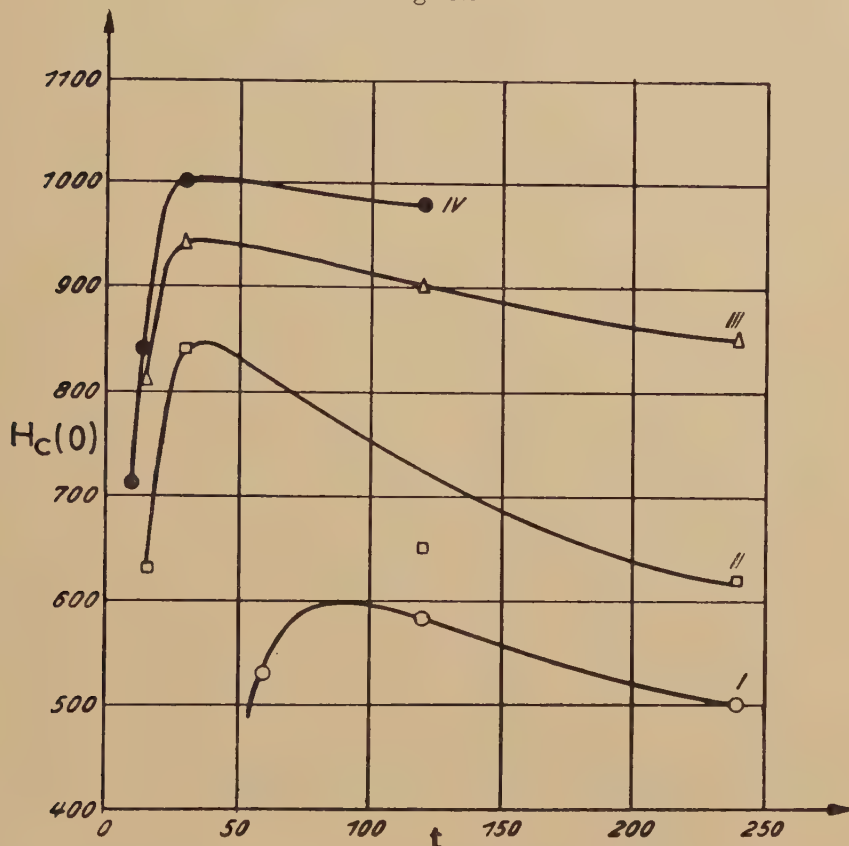
Size dependence of coercivity of iron and cobalt.  $H_c$ , coercive force;  $d$ , particle diameter in microns. After Meiklejohn (1953).

formate decomposes more rapidly than the iron salt the reduction to the final alloy powder takes place more rapidly than is the case for pure iron. The coercive force maxima thus occur at lower reduction times, followed by a less rapid decay, the maximum values themselves being raised by increasing the cobalt content. These three results are summarized in fig. 3.3, and they imply that Fe–Co powders are much more attractive as permanent magnet materials than those composed of pure iron. The increase of  $H_c(0)$  with increasing Co content has itself never been fully investigated.



The addition of cobalt to iron lowers the magnetocrystalline anisotropy, which vanishes at about 45% Co, and raises the saturation magnetization, so that the coercivity change on alloying may be due, at least in part, to an increase of the effective shape anisotropy (see also Luborsky *et al.* 1958).

Fig. 3.3



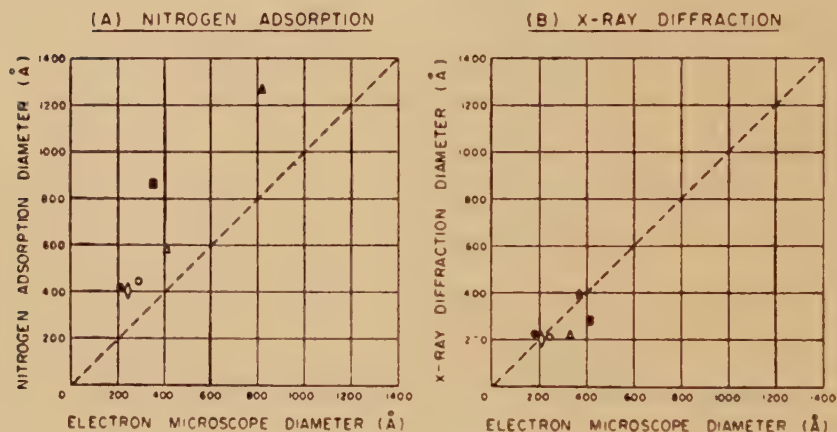
Dependence of coercivity of Fe-Co powders on reduction time.  $H_c(0)$ , coercivity at infinite dilution;  $t$ , reduction time, minutes; cobalt contents: I, 0%; II, 10.5%; III, 26.3%; IV, 36.4%. After Lihl (1953).

Anantharayanan and Libsch (1953, cf. also Libsch and Conard 1954), prepared iron powders by the reduction in hydrogen of the oxide  $\alpha\text{Fe}_2\text{O}_3$ . The compacts prepared from these powders, with a particle size about  $0.02\mu$  and a coercivity about 550 oersted, were then reheated for 2 hours in hydrogen at various temperatures; the coercivity was found to drop rapidly to low values at about  $600^\circ\text{C}$  where rather complete sintering was thought to take place. Stewart, Conard and Libsch (1955) prepared fine iron powders by formate reduction and in the presence of up to 10% additional formates or oxides of Mg, Cd or Sn. These were found to retard

the degree of sintering and the degree of reduction, leading to an increase of maximum energy product, which reached  $0.8 \times 10^6$  gauss-oersted for a compact of density 4.3. The change of coercive force with the reduction temperature of these powders was much less rapid in the presence of the additionals, which acted as effective dispersion agents.

Similar investigations on the production of metal and alloy powders with or without additionals have also been reported by H. Kojima (1955a). Carman (1955a) produced iron powders by the low temperature ( $250^\circ$ – $350^\circ\text{C}$ ) reduction of commercial iron oxides. He found by means of electron microscope observation that there is a qualitative correlation between the shapes and sizes of the starting material and the final metal powder, a result confirmed later by Franklin and Campbell (1955, see below).

Fig. 3.4

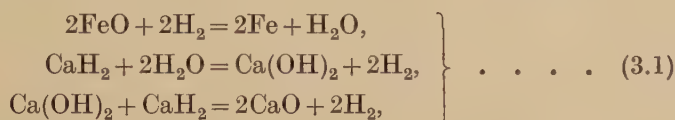


Comparison of x-ray,  $\text{N}_2$  adsorption and electron microscope particle sizes for Fe and Fe-Co. After Franklin *et al.* (1953).

Whereas in these investigations the main purpose remained the measurement of the magnetic properties of powder materials produced under various conditions, other investigations had as their aim the more accurate measurement of particle size, thus extending the original French investigations in this direction. Kopelman (1952, cf. also Schubert and Kopelman 1952) compared particle sizes for iron powders obtained from x-ray line broadening (see also Wilchinsky 1951) with those obtained from nitrogen adsorption isotherms, using the Brunauer–Emmett–Teller technique. The values obtained by the second method were found to be larger than those by the first. A systematic investigation using these two and, in particular, electron microscope studies of iron and Fe–Co powders was carried out by Franklin *et al.* (1953). Particle dispersion was carried out by means of the combined action of mechanical forces and alternating magnetic fields,

giving reasonable results; all clusters were, however, not eliminated. The electron microscope pictures showed the particles to be almost spherical and were used to carry out a statistical particle size analysis. In all cases the measured sizes were compared with those obtained from line broadening and nitrogen adsorption, and the results are shown in fig. 3.4. Whereas the x-ray and electron microscope values agree well, the adsorption values deviate as in Kopelman's measurements, perhaps due to the presence of incompletely reduced oxides which would not be detected by the x-ray or electron microscope observations.

Later measurements by Franklin and Campbell (1955) were on iron particles produced by the low temperature ( $125^{\circ}$ – $450^{\circ}\text{C}$ ) reduction of iron oxides. The reduction of FeO could be completed at temperatures as low as  $125^{\circ}\text{C}$ , where sintering is negligible, by carrying out the process in the presence of  $\text{CaH}_2$ :



the amount of metallic iron produced being measured by the amount of  $\text{H}_2$  gas evolved. The sizes of the oxide particles  $d_0$  and of the iron particles  $d_{\text{F1}}$  were measured as above, calculated values  $d_{\text{F2}}$  being obtained from  $d_0$  assuming each oxide crystal to produce one iron particle without change of shape. The values of these diameters are shown in table 3.1. The results are for iron produced from FeO, as well as from other oxides which, it is stated, are polycrystalline, the value of  $d_0$  referring to the crystallites (cf. also Osmond 1953, Campbell 1957, Luborsky *et al.* 1958). The close correspondence between  $d_{\text{F1}}$  and  $d_{\text{F2}}$  confirms the result of Carman (1955 a).

Table 3.1. Observed and calculated iron particle diameters.  $d_0$ , oxide crystal diameter;  $d_{\text{F1}}$ , iron particle diameter obs.;  $d_{\text{F2}}$ , iron particle diameter, calc. from  $d_0$ . After Franklin and Campbell (1955)

Material	$d_0(\mu)$	$d_{\text{F1}}(\mu)$	$d_{\text{F2}}(\mu)$
FeO	0.035	0.025	0.027
	0.021	0.017	0.016
	0.010	0.010	0.008
$\text{Fe}_3\text{O}_4$	0.028	0.020	0.022
$\gamma\text{-Fe}_2\text{O}_3$	0.036	0.028	0.026
$\alpha\text{-Fe}_2\text{O}_3$	0.043	0.033	0.033

### 3.3. The Production and Properties of Elongated Particles

The electron microscope pictures of Meiklejohn (1953), Franklin *et al.* (1953) and others show that the metal powder particles prepared prior to 1955 by the methods described above (reduction of salts or oxides, electro-deposition into mercury) are produced with an almost spherical shape.



For this reason it was not possible to take full advantage of the potential benefits of large shape anisotropy. This would lead to an increase of coercive force and, since elongated particles should be amenable to magnetic alignment, to an increase of remanence in the alignment direction. Both these factors would then be able to improve the maximum energy product beyond the best values (about  $1.5 \times 10^6$  gauss-oersted) obtained for near spherical powders. In 1955 a method of producing elongated powders was developed by Paine *et al.* (1955 a), and the expected improvement was attained.

The method used was a modification of electrodeposition into a mercury cathode. The anode was an iron ingot and the electrolyte a dissolved iron salt such as the chloride, kept slightly acid to keep the cathode surface clean. The major innovation consisted in keeping this surface free from mechanical disturbances, thus allowing the growth of elongated particles. After a first magnetic separation of the iron particles from the mercury, the slurry is heat treated for a short time at about  $200^\circ\text{C}$ ; this has the effect of removing dendritic outgrowths which are observed on the surfaces of untreated particles (see below). The particles are then coated by adding a trace of tin, zinc, or other metal which acts as an effective dispersion agent. Further separation from the mercury is carried out by surface oxidation and finally by washing and heating *in vacuo* at about  $250^\circ\text{C}$  for some hours. The particles are then dispersed in a molten thermoplastic binder and compressed and moulded in the presence of a high magnetic field which is kept on until the binder has set. Some of the many possible shapes which may be prepared by these methods are illustrated in fig. 3.5 (Pl. 1). The technical properties of these magnets have been described by Lever *et al.* (1958), who give demagnetizing curves for iron and Fe-Co compacts, with maximum energy products up to 3.5 and  $5 \times 10^6$  gauss-oersted respectively. The curves may be readily altered by varying the degree of compression. Among other useful properties of these magnets are a low temperature coefficient of remanence, magnetic stability and good mechanical behaviour such as machineability and solderability.

The scientific investigation of these elongated particles has been described in a series of papers by Paine and his associates. Mendelsohn *et al.* (1955) describe the results of electron microscope observations, which enable the dimensional ratios of the particles to be estimated, these being found to be in general correlation with the coercive force, table 3.2. This also shows the effect of particle alignment on the coercive force, which is otherwise demonstrated by the fact that the reduced remanence in the preferred direction  $I_r''/I_0$  can take up values up to about 0.9. The effect of compression on coercive force was also investigated. Néel's formula (2.2) was found to break down when the packing factor exceeded about 0.4.

Further results on iron particles are reported by Paine *et al.* (1955 b). Figure 3.6 (Pl. 2) shows an electron microscope picture of particles with mean diameter  $0.014 \mu$ , mean dimensional ratio 3.0 and coercive force

1600 oersted. The strongly serrated edges of some of the particles, further developed into dendrites in others, are clearly visible. The magnetic measurements verify the importance of shape anisotropy. Torque curves show that the particle anisotropy is uniaxial. The temperature variation of the coercive force indicates that whereas for round particles this variation is large, implying predominant magnetocrystalline anisotropy, increasing elongation results in a decrease of the temperature coefficient, implying a greater importance of shape anisotropy. The coercivity itself, although it may be above 2000 oersted, is still lower than the values predicted by the simple theory discussed in § 2. It is this result, together with the observation of serrated edges illustrated in fig. 3.6 (Pl. 2), which led Jacobs and Bean (1955) to develop their chain-of-spheres model which involves incoherent magnetization reversals and hence a decrease of the coercive force (cf. § 2). As Paine *et al.* (1955 b, cf. also § 2 and Wohlfarth 1956) point out, such decreases may also be due to a variety of other reasons.

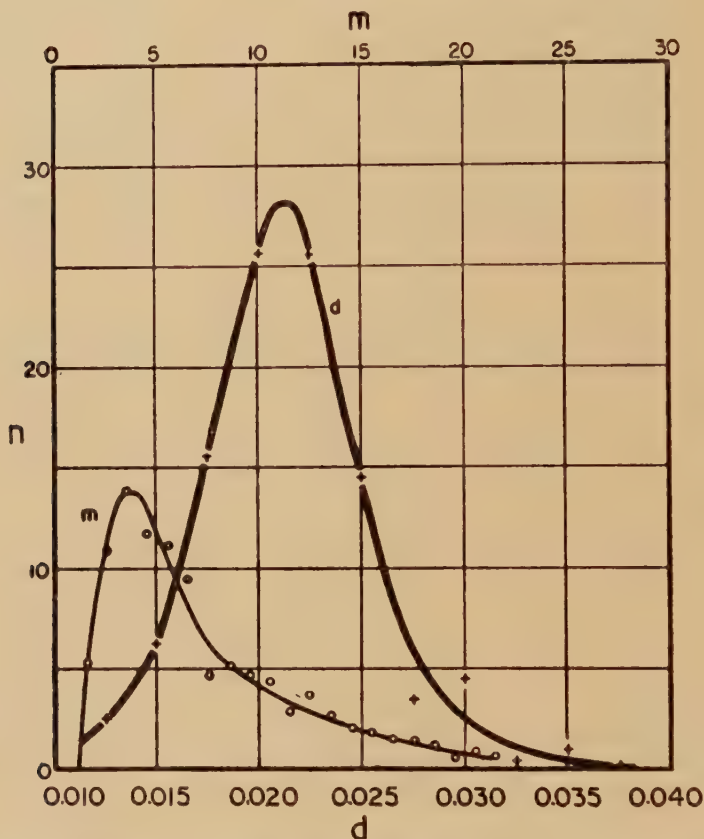
Table 3.2. Coercive force of elongated iron particles.  $d$ , mean diameter;  $m$ , mean dimensional ratio;  $H_c^{\parallel}$ ,  $H_c^{\perp}$ , coercive forces parallel and perpendicular to preferred direction. After Mendelsohn *et al.* (1955)

$d(\mu)$	$m$	$H_c^{\parallel}$ (oersted)	$H_c^{\perp}$ (oersted)
0.014	1.3	1090	1090
0.015	2.7	1600	1080
0.018	4.5	2050	1800

Luborsky *et al.* (1957) have extended these measurements to Fe-Co particles with about 40% Co. Figure 3.7 shows their distribution curves for diameter and dimensional ratio. These were obtained from electron microscope observations which show, incidentally, that these particles have fewer dendrites than was the case for the iron particles described above. The following magnetic measurements were carried out: (1) Variation of coercivity with angle  $\theta$  relative to the preferred direction. For the cobalt-iron as well as for iron particles the  $H_c, \theta$  curves have a slight maximum near  $\theta = 55^\circ$ , which was taken to imply an incoherent rotation mechanism of magnetization (Jacobs and Bean 1955, Shtrikman and Treves 1959, but see also Wohlfarth 1959). (2) Temperature variation of coercivity. This is small, but has a sign opposite to that for the iron particles and of the shape anisotropy coefficient. Luborsky *et al.* (1958) ascribe this result to the partial alignment of [111] crystallite axes parallel to the major axes of the particles, and a resulting small contribution from magnetocrystalline anisotropy. (3) Reduced remanence. Values up to 0.9 were obtained for aligned and between 0.5 and 0.66 for non-aligned

particles. For the last the reduced remanence increases on compacting, due presumably to some mechanical alignment, the particles being forced into a plane perpendicular to the pressing direction. (4) Variation of coercivity with compression. As for the iron particles, there are deviations from a linear dependence, which are ascribed to particle coalescence.

Fig. 3.7



Distribution curves for elongated Fe-Co particles.  $n$ , percentage distribution;  $d$ , diameter in microns;  $m$ , dimensional ratio. After Luborsky *et al.* (1957).

Further measurements, and also some theoretical work, on iron and Fe-Co (40% Co) particles are reported by Jacobs and Luborsky (1957). The angular variation of coercivity was considered for a partially aligned assembly of chain-of-spheres particles undergoing incoherent rotations, a fraction  $g$  being taken to be completely aligned and the rest randomly oriented in space or in a plane. The perpendicular coercivity  $H_c^\perp$  increases quite rapidly as  $g$  decreases from 1, and the maximum in the  $H_c(\theta)$  curve tends to be suppressed at the same time (cf. also Wohlfarth 1959). From measurements of the high field torque curves (up to  $2 \times 10^4$  oersted) the



effective particle anisotropy energy  $K$  was estimated and compared with results for coherent rotation models with which they agree quite well. Observed values of  $K$  range to  $6 \times 10^6 \text{ erg cm}^{-3}$  for iron and to  $7 \times 10^6$  for Fe-Co particles. Jacobs and Luborsky also discuss results of related rotational hysteresis measurements (cf. § 2). The maximum field beyond which the energy  $W_r$  is negligibly small is closely related to the maximum anisotropy energy of the particles  $K$ , but, owing to anisotropy variations, only order of magnitude agreement is attained. The maximum fields observed lie in the range 4 to  $7 \times 10^3$  oersted. Finally, from measurements of the rotational hysteresis integral  $R$ , defined by relation (2.11), it was concluded that, since  $R$  has values much larger than those calculable for coherent rotations, these are in fact more nearly incoherent.

In the work just discussed electron microscopy served as a valuable aid in interpreting magnetic measurements. A series of papers by Freeman and Watson describes electron microscope observations *per se*. Watson and Freeman (1956a, b) prepared iron crystals by electrolytic methods and found that their dendritic structure could be varied according to the method of preparation (see also Paine *et al.* 1955a). The central stem of each particle was found to consist of many single crystallites (see also Luborsky *et al.* 1958), and platelets were observed to occur in both the main stems and the side branches. By using more refined techniques (Watson 1957a), Freeman and Watson (1957) found that the ultimate crystallites are rhombic dodecahedrons of size 0.01 to  $0.05 \mu$ , and that needles or chains of these crystals are formed by diagonal attachment. From this 1-dimensional structure three secondary branches may appear growing in a regular manner from any point of the primary, the secondaries themselves being composed of crystallites and having in some cases their own tertiary outgrowths. From the point of view of magnetic hardness large dendritic particles are less satisfactory than smaller ones whose side branches have by some means been reduced. Where this is possible needle-shaped particles may be produced, and studied electron microscopically, the lengths being roughly  $0.3 \mu$  and the dimensional ratios as high as 20 or above. For some of these 'better' particles short side branches less than  $0.03 \mu$  in length were still present. Some of the specimens had been oxidized to a small extent to  $\text{Fe}_3\text{O}_4$ , with, in general, an increase of dendritic growth and a decrease of coercivity. The coercivity results may be interpreted directly in terms of particle size and, more subtly, in terms of a decrease of the effective shape anisotropy due to the side branches.

Watson (1957b) has extended these experiments by observing the degree of alignment of the iron particles in magnetic fields up to  $2.5 \times 10^4$  oersted. The particles were suspended in butyl methacrylate which was allowed to polymerize in the field, after which microtome sections were obtained and studied. It was found that although some macroscopic alignment could be induced by the field, the particles themselves formed chain-like or circular clusters within which there was little evidence of alignment. These clusters form so as to reduce the total magnetostatic

energy, the magnetic field being unable to overcome this tendency. Watson *et al.* (1958) found that for strongly dendritic particles the aligning field may act more strongly on the side branches than on the main stems, so that the latter may even be aligned perpendicular to the orienting field.

The formation of chain-like clusters of ferromagnetic metal powders had been reported previously by Beischer and Winkel (1937) for nickel and iron aerosols, and by Courtney (1955) for nickel particles reduced in the presence of a magnetic field.

### 3.4. *Oxide Coated Powders Exhibiting Exchange Anisotropy*

Meiklejohn and Bean (1956, 1957) observed that small cobalt particles coated with a cobalt oxide shell exhibit unusual magnetic properties. The particles, of size  $0.02\mu$ , were produced electrolytically in mercury, surface oxidized in air and cooled to low temperatures in the presence of a strong magnetic field. They had the following properties: (1) From torque measurements the anisotropy was found to be unidirectional. (2) The hysteresis loop for the particles cooled in a field is displaced along the field axis giving a great improvement in permanent magnet properties, e.g.  $H_c = 3700$  oersted in the second, cf. 500 oersted in the first quadrant, and a reported maximum energy product  $4 \times 10^6$  gauss-oersted. If the particles are cooled to low temperatures in the absence of a field the hysteresis loop is symmetrical, with more inclined sides and a coercive force 1200 oersted; both loops are shown in fig. 3.8. This phenomenon is closely related to the unidirectional anisotropy of the particles (Meiklejohn and Bean 1957, Wohlfarth and Tonge 1957), the displaced loop being a composite one due to the uniaxial anisotropy of the cobalt and the unidirectional anisotropy resulting from the presence of the oxide shell. (3) The rotational hysteresis reaches a finite saturation value in high fields, in contrast to the zero saturation value of pure metallic powders.

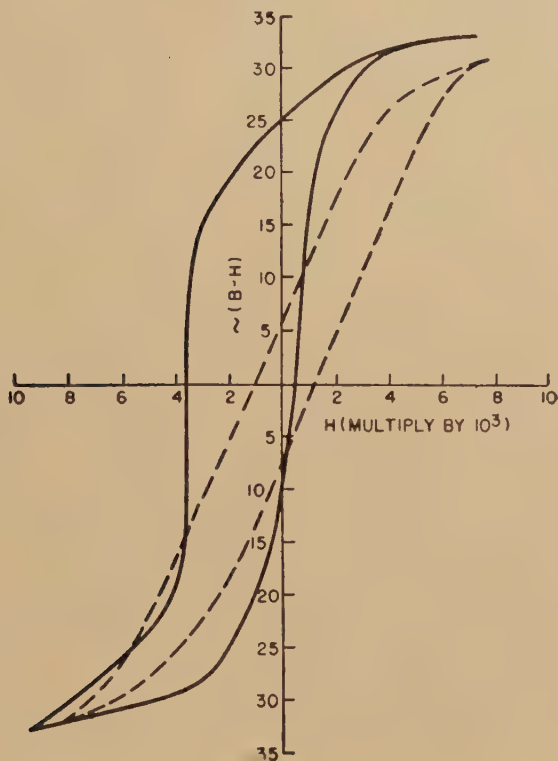
The results are interpreted in terms of an 'exchange' anisotropy between the ferromagnetic cobalt and the antiferromagnetic oxide phases. By measuring the loop shift as a function of temperature it was found that the effect vanishes in the neighbourhood of the Néel point of CoO,  $290^\circ\text{K}$ . Removal of the oxide layer by reduction also causes loop symmetry, but a shift could again be induced by prolonged re-oxidation.

Similar results have also been observed (Meiklejohn 1958) in Fe-FeO particles, whose saturation rotational hysteresis vanishes at the Néel point of FeO. Newkirk and Martin (1957) investigated by electron diffraction the crystallographic relationship between cobalt and cobalt oxide in the coated particles. The oxide was found to be partially oriented, with (111) planes parallel to the basal planes of the metal. For Ni-NiO particles no displaced loops have been observed; here the oriented part of the oxide was found to have an orientation of (111) planes of the metal. The exchange anisotropy finds some explanation in these relative orientations.

If the co-existence of ferromagnetic and antiferromagnetic phases can lead to these unusual magnetic properties for oxide coated particles,

then similar results might be expected for other materials where there is evidence of such a co-existence. Shifted hysteresis loops have been observed in  $\text{UMn}_2$  (Lin and Kaufmann 1957), disordered  $\text{Ni}_3\text{Mn}$  (Kouvel *et al.* 1958, cf. also Kouvel *et al.* 1959) and  $\text{LaFeO}_3$  (Watanabe 1958, unpublished and acknowledged with thanks) at temperatures below the Néel points of the antiferromagnetic phases. From the point of view of application as permanent magnet materials it is essential to have a material whose antiferromagnetic phase has a high Néel temperature.

Fig. 3.8



Hysteresis loops of  $\text{Co}+\text{CoO}$  particles at  $77^\circ\text{K}$ . Full curve, cooled in a high field; broken curve, cooled without a field. After Meiklejohn and Bean (1956, 1957).

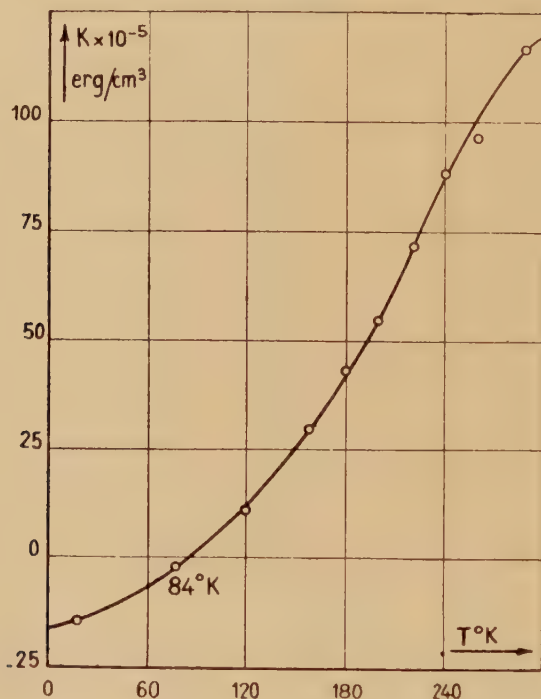
### 3.5. Iron-Platinum and Cobalt-Platinum Powders

The properties of the permanent magnet materials in the alloy systems  $\text{Co-Pt}$  and  $\text{Fe-Pt}$  are discussed in § 8, where it is shown that the cause of magnetic hardness is to be found in the face centred tetragonal crystal structure of the ordered equiatomic phases. Weil (1948 c, 1949 c) prepared powder magnets with these compositions and obtained remarkable magnetic properties. He reduced the compound  $\text{CoPt}(\text{CN})_4$  for 1 to 2 hours in hydrogen at  $500^\circ$  to  $600^\circ\text{C}$ , followed by pressing and sintering at a higher temperature about  $1000^\circ\text{C}$ . The resulting material was found



to be crystallographically ordered with a face centred tetragonal structure. Magnetic properties include  $H_c = 8 \times 10^3$  oersted (but  $_B H_c$  only  $4.7 \times 10^3$  oersted),  $B_r = 6.2 \times 10^3$  gauss and  $(BH)_{\max} = 7.8 \times 10^6$  gauss-oersted. An FePt powder magnet produced similarly had a coercive force as high as  $2 \times 10^4$  oersted (but  $_B H_c$  only  $1.9 \times 10^3$  oersted and  $(BH)_{\max}$  only  $1 \times 10^6$  gauss-oersted). Although, as discussed in § 8, the high coercivity of the cast alloys may be due in part to strain effects, this is unlikely in the case of the powders. Here the high coercive force is most likely due to the extraordinarily high magnetocrystalline anisotropy resulting from the lattice tetragonality. A very rough estimate of the anisotropy constant  $K$  required to account for the observations on FePt powders is  $2 \times 10^7$  erg cm $^{-3}$ , agreeing well with Martin's (1957) estimate for CoPt,  $1 \times 10^7$ . Powdered CoPt alloys seem to have found some use industrially (Mendelsohn 1958).

Fig. 3.9



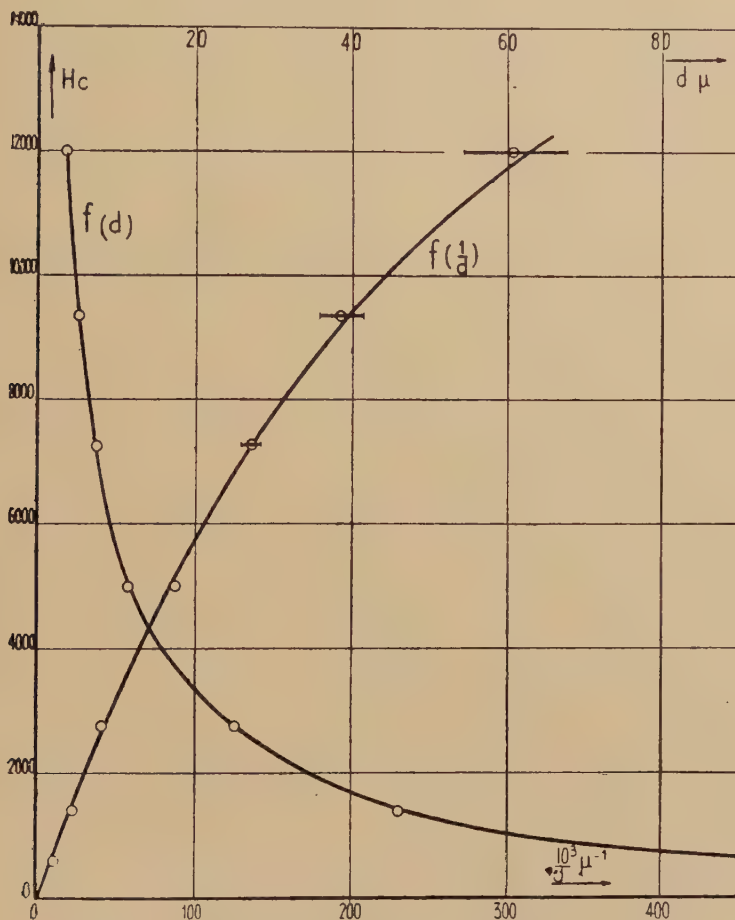
Temperature variation of anisotropy constant of MnBi.  
From Guillaud (1949 b).

### 3.6. Manganese-Bismuth Powders

The most extensive experimental investigations on MnBi powders are those of Guillaud (1943, 1949 b, but see also Thielmann 1940). An account of a method of preparation is given by Société d'Ugine (1948 b). A binary alloy was produced by melting manganese and bismuth powders in a

furnace either at high ( $700^{\circ}$ – $1250^{\circ}\text{C}$ ) or low temperatures (about  $300^{\circ}\text{C}$ ), followed by a heat treatment of the ingots between  $150^{\circ}$  and  $600^{\circ}\text{C}$  for from 2 to 100 hours. The alloy was then crushed down to prepare very fine powders, followed by magnetic separation of the strongly magnetic from any unreacted phases, and finally by magnetic alignment and compression in the presence of a binder.

Fig. 3.10



Size dependence of coercive force of MnBi. From Guillaud (1949 b).

In 1949 Guillaud summarized his results (1943) for MnBi powders produced by these methods. By carrying out magnetization measurements over a wide range of temperature and field strength and along and perpendicular to the preferred direction he obtained the temperature variation of the magnetic anisotropy coefficient  $K = K_1 + K_2$ . The results are shown in fig. 3.9, indicating an isotropy point at  $84^{\circ}\text{K}$ . An estimate

of  $K_1$  and  $K_2$  separately was made by magnetic measurements at room temperature, where  $K_1 = 8.9 \times 10^6$ ,  $K_2 = 2.7 \times 10^6$  erg cm<sup>-3</sup>. Guillaud also measured the room temperature coercive force parallel to the preferred direction as a function of grain size (between 3 and 60  $\mu$ ), the results being shown in fig. 3.10. The highest coercivity observed ( $1.2 \times 10^4$  oersted) was obtained for the 3  $\mu$  particles, and considerably higher values are expected if further size reductions were possible. The qualitative relation of these enormous coercive forces with the high magnetocrystalline anisotropy is easily understood, but the size dependence remains an unsolved problem (cf. § 2). Measurements are also reported of the temperature variation of the coercivity and remanence, which both vanish at the isotropy point. These two quantities vary greatly with direction; for the 3  $\mu$  powders investigated at room temperature, the respective values of the coercivity and remanent moment per unit mass perpendicular to the preferred direction are only 200 oersted and 0.7 e.m.u.g<sup>-1</sup> (cf. 64.0 e.m.u.g<sup>-1</sup> in the parallel direction), showing that the magnetic alignment of the particles is nearly perfect. For an isotropic powder both the coercivity and remanence are approximately equal to half the values of an anisotropic powder and measured in the preferred direction; these are results in agreement with simple theory. For a powder with larger grains the results are less perfect due, presumably, to domain wall effects. Little has been done on the compression dependence of the coercive force, although Société d'Ugine (1948 b) report this dependence to be small as for cobalt powders (Weil 1951 a) and as expected (Wohlfarth 1955 a) if the coercivity is determined by the magnetocrystalline anisotropy.

Although Guillaud stressed the importance of MnBi as a possible permanent magnet material it was left to Adams and associates to make substantial progress in this direction (Adams *et al.* 1952 a, b, Adams 1953). The magnets were prepared as follows: As with Guillaud, finely divided manganese and bismuth powders were reacted to form an alloy; they were heated in a rotating furnace in a He atmosphere for 5 hours at 700°C. This was followed by a further anneal at 440°C for 16 hours, increasing the grain size. After removal of excess liquid bismuth the alloy was cooled to room temperature. Pulverization and enrichment was carried out by a hammer mill in the presence of He gas and further sieving and by magnetic separation. Magnets with 90% pure MnBi could be produced by this means. During the final compacting and alignment, in magnetic fields up to  $2 \times 10^4$  oersted, any unreacted bismuth could act as a partial dispersion agent. Some experimental results were obtained on the pressure dependence of the coercive force of the compacts. As pointed out, this is expected to be weak, but Adams found that for a compact of density 6.6,  $H_c = 7.7 \times 10^3$  oersted, while for one with density 7.5,  $H_c = 4.6 \times 10^3$  oersted. This large change was suspected to be due to better particle alignment and less sintering at the lower density, but the first explanation seems ruled out by the fact that the remanence of the two specimens is almost the same,  $B_r = 3.4 \times 10^3$  gauss.



By such methods Adams was able to prepare the permanent magnet material 'Bismanol' with density 8.1,  $B_r = 4.3 \times 10^3$  gauss,  $H_c = 7 \times 10^3$  oersted (but  $BH_c$  only  $3.4 \times 10^3$  oersted) and  $(BH)_{\max} = 4.3 \times 10^6$  gauss-oersted. Adams and Hubbard (1953) describe several ways of improving these figures, by a more effective removal of excess bismuth, pulverization, compacting and alignment. The best permanent magnet material, with  $(BH)_{\max} = 5.3 \times 10^6$  gauss-oersted, had a density 6.7, effective particle size (obtained from fig. 3.10)  $9.5 \mu$ , particle alignment (from the remanence) 90% and purity 90%. This maximum energy product does not yet approach Guillaud's estimate  $18 \times 10^6$ , but the manganese-bismuth permanent magnet material is nevertheless of great potential usefulness. Adams and Hubbard (1953) also investigated the effects of temperature variations, with reference to fig. 3.9, shock, humidity and other physical influences, and Adams (1957) investigated the effects of corrosion in greater detail.

A series of investigations on MnBi has also been reported by Shur and associates. Shtoltz and Shur (1954) reported coercivity and remanence measurements of oriented material with grains between 3 and  $250 \mu$  at  $20^\circ$  and  $-195^\circ\text{C}$ . At the lower temperature  $H_c$  was low, about 70–150 oersted and the reduced remanence about 0.08 and almost independent of particle size and orientation. These results demonstrate clearly the effect of the vanishing of the anisotropy at low temperatures (cf. fig. 3.9). Shur *et al.* (1957a) obtained almost perfect particle alignment with  $9 \mu$  MnBi particles for which the room temperature parallel coercivity was reported as  $1.09 \times 10^4$  oersted, above Guillaud's value, and the reduced remanence as 0.99; the perpendicular values were given as 700 oersted and 0.035 respectively. Shur (1959) refers to further work from his laboratory and describes, in particular, some Bitter pattern investigations on MnBi particles. For small single domain particles the colloid was found to collect round the edges where the magnetic pole strength is most intense; the magnetization change in external fields is one of pure rotation, demonstrated by a displacement of the colloid. For larger particles the magnetization process in relatively weak fields is by the formation, initially at the surface, and subsequent movement of domain walls, leading to a rather low coercive force only a few hundred oersted; in strong fields the nuclei of reverse magnetization are inhibited and magnetization proceeds by rotation with a high coercive force several thousand oersted (see also Shur *et al.* 1957). Shur (1959, see also Shur *et al.* 1957b) also obtained magnetization curves of aligned MnBi particles at room temperature and near the isotropy point.

Apart from experimental work related directly to the magnetic hardness there is now a series of papers on the more general properties of Mn-Bi. Williams *et al.* (1957, see also Volkov 1954) reported measurements of the magnetostriction coefficient  $\lambda$  and magnetocrystalline anisotropy constants  $K_1$  and  $K_2$  for oriented polycrystalline MnBi specimens. The values of  $\lambda$  are largest if measured parallel to the field which is applied perpendicular

to the hexagonal crystal axes; the extrapolated saturation value is  $-8 \times 10^{-4}$ . Domain patterns on compacts were observed by Roberts and Bean (1954) and by Andrä (1956a) using the Kerr effect. Andrä's measurements extend to low temperatures where changes of the domain structure were observed due to the decrease of the magnetocrystalline anisotropy (cf. fig. 3.9). Ellis *et al.* (1957, 1958) prepared single crystals of MnBi by crystallization from a liquid solution in a temperature gradient, and drew conclusions on subgrain structure from Bitter patterns. The crystals used (one specimen is quoted as having dimensions  $4 \times 7 \times 12$  mm) may well be more suitable for fundamental magnetic investigations than oriented polycrystalline specimens. Boothby *et al.* (1958) found that when a strong magnetic field about  $8 \times 10^3$  oersted is applied during the heat treatment of a random polycrystalline MnBi specimen, orientation of the crystallites is accompanied by recrystallization. Earlier Roberts (1955) had observed the growth in a magnetic field of columns of highly oriented crystallites and ascribed this phenomenon to either a magnetically enhanced nucleation process at the tips of the columns, or to a diffusion process of MnBi particles to these tips.

Only reference can here be made to the experiments of Williams *et al.* (1957, cf. also Williams and Sherwood 1958) on thin films of MnBi using the Faraday effect, to the neutron diffraction studies of Roberts (1956) and the magnetic and structural investigations of Heikes (1955).

#### § 4. IRON OXIDES AND RELATED POWDER MATERIALS

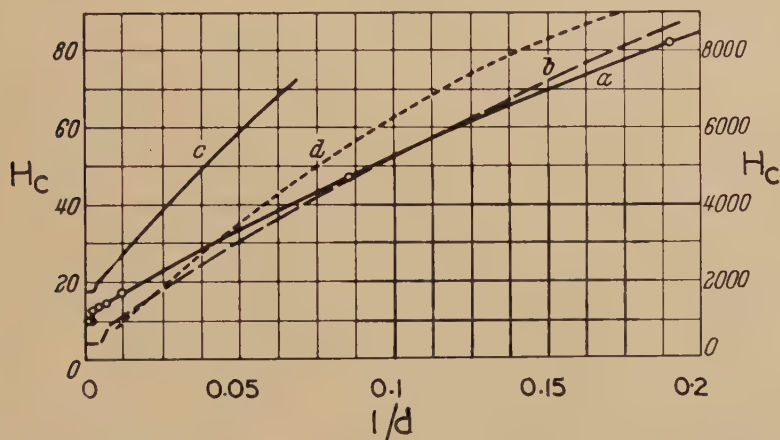
Magnetically hard iron oxide powder materials have received an extraordinary amount of attention due to their great practical importance. The oxides  $\text{Fe}_3\text{O}_4$  (magnetite) and  $\alpha\text{Fe}_2\text{O}_3$  (haematite) are common constituents of rocks, and the oxide  $\gamma\text{Fe}_2\text{O}_3$  is especially important as the most widely used magnetic component of magnetic tapes. It seems impossible to give full references to the vast literature, but this is the more unnecessary as several useful reviews of the technical aspects of the properties of iron oxides already exist. The magnetochemistry of iron oxides has been discussed by Selwood (1956) who gives full references to the earlier work. Magnetic tape recording has been reviewed by Spratt (1958) and the literature up to 1952 has been surveyed by Wilson (1956). Reviews of rock magnetism have been published by Nicholls (1955), Néel (1955a), Runcorn (1955), Blackett (1956) and Blackett *et al.* (1957).

##### 4.1 $\text{Fe}_3\text{O}_4$ and $\gamma\text{Fe}_2\text{O}_3$ : Size Dependence of Magnetic Properties

Although coercive force measurements on magnetite powders had been reported for many years, one of the earliest systematic studies seems to be that of Gottschalk (1935, 1941), who measured coercivity as dependent on grain size for ground artificial and natural specimens. The particle sizes  $d$  ranged down to about  $3\mu$ , and the coercivity was found to depend linearly on  $1/d$ , reaching values up to about 130 oersted. De Vaney and Coghill (1938) investigated magnetite grains with size between 14 and  $300\mu$  and also established a  $1/d$  dependence of coercive force as well as a

linear relation between this and the work input during the grinding operation. Sappa (1937) extended the range of grain sizes down to about  $1.5\mu$ , and obtained coercive forces up to about 260 oersted. The inverse dependence on grain size was found to break down for the smallest particles, and Sappa believed that  $H_c$  would reach a finite value about 300 oersted in the limit of zero grain size. All these and many other measurements up to 1939 were reviewed by Koenigsberger (1947). Herroun (1943) reported results for solid and powdered magnetite specimens from different natural sources and coercivities up to 190 oersted. Torkar *et al.* (1958) prepared magnetite powder fractions from an ore and determined the average size of each fraction microscopically. Figure 4.1 shows the variation of the measured coercive force with the inverse grain size  $d$ , including, for comparison, the results of Gottschalk (1935) and de Vaney and Coghill (1938) for magnetite as well as those of Guillaud (1943) for MnBi (cf. § 3). The results were explained in terms of a finite magnetically inactive surface layer, but this interpretation seems doubtful in view of the results of Luborsky (1958 a).

Fig. 4.1



Size dependence of coercivity. Curves *a*, *b*, *c*,  $\text{Fe}_3\text{O}_4$ ; curve *d*, MnBi. Left-hand scale for *a*, *b*, *c*; right-hand scale for *d*.  $H_c$ , coercivity; *d*, particle diameter in microns. After Torkar *et al.* (1958).

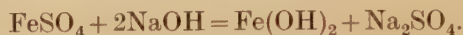
Magnetic measurements on very small colloidal  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{Fe}_2\text{O}_3$  particles were reported by Elmore (1938). The magnetization curves could be fitted to a Langevin formula only if a Gaussian variation of sizes was assumed, the mean diameter of the two colloids being about  $0.20\mu$ . This work is one of the earliest investigations of superparamagnetism in tiny grains (see also §§ 2 and 6 and the review of Bean 1959). Similar measurements on  $\gamma\text{Fe}_2\text{O}_3$  aerosols were also reported by Haul and Schoon (1939) and Knappwost (1957 a) who investigated particles with diameters about  $0.003\mu$ .



In addition to measurements on pure oxides similar results were also obtained on other related minerals, for example titanomagnetite (Akimoto 1955).

#### 4.2. *Magnetochemistry and Applications to Magnetic Tapes*

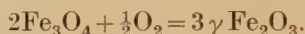
Two types of  $\gamma\text{Fe}_2\text{O}_3$  powders have been used as magnetic recording media, namely small isotropic powders and larger elongated ones. The method of preparation of the first type of substance (frequently called equant or non-acicular) has been described by Ranger (1947) and Krones (1955). One of many variants is to start with ferrous sulphate which is dissolved in water and transformed to the hydroxide, according to



The hydroxide, precipitated as a finely divided powder, is then oxidized to magnetite by means of an oxidizing agent such as sodium nitrate, the process taking place at about  $80^\circ\text{C}$  and the magnetite being formed as a black precipitate, according to



The black oxide is then washed and dried and oxidized in air at about  $300^\circ\text{C}$  to form brown  $\gamma\text{Fe}_2\text{O}_3$  particles,



Oxidation at higher temperatures, above about  $550^\circ\text{C}$ , transforms the unstable  $\gamma$  to the stable  $\alpha\text{Fe}_2\text{O}_3$ . The  $\gamma\text{Fe}_2\text{O}_3$  so produced was shown by electron microscopy (Krones 1955) to form roughly cube shaped grains with size about  $0.1\mu$ . The many other possibilities of preparing oxide powders for tape production, requiring the use of a plastic binder and base film, have usually been described only in patent specifications. The early German tapes using non-acicular particles usually had a coercive force of less than 100 oersted, but more recently considerably higher coercivities have been attained for this type of powder by the admixture of cobalt. Agfa (1954) describe the preparation of a material containing small amounts (2–7%) of cobalt sulphate as an additional in the above process, during which it appears that cobalt ferrite is formed and the coercive force is raised to over 1000 oersted (cf. also § 5).

Elongated or acicular  $\gamma\text{Fe}_2\text{O}_3$  powders for tape manufacture are produced in a different way, by a cycle of reduction and oxidation of either red  $\alpha\text{Fe}_2\text{O}_3$  or yellow  $\alpha\text{FeO.OH}$  acicular particles (Armour Research Foundation 1952). The reduction to form magnetite may take place at about  $440^\circ\text{C}$  in hydrogen, and the subsequent re-oxidation to  $\gamma\text{Fe}_2\text{O}_3$  at about  $200^\circ\text{C}$  in air. These details may be varied in many ways, but it appears that the final brown oxide powders usually have the same shape and size as the starting material. Krones (1955) shows an electron microscope photograph from which the final oxide particles are seen to have a length about  $1\mu$  and axial ratio about 10, but, according to Armour (1952), the

lengths may vary from  $0.25$  to  $1.5\mu$  and the widths from  $0.1$  to  $0.3\mu$ . The coercive forces quoted range from 200 to over 300 oersted. The particles, being acicular, may be oriented magnetically during some stage of tape manufacture, leading to anisotropy in the magnetic properties.

The oxidation-reduction process has also been investigated by H. Kojima (1954). He measured the coercive force  $H_c$  of  $\text{Fe}_3\text{O}_4$  powders ( $H_c = 100$  oersted), oxidized at various temperatures. He found that  $H_c$  increases to over 200 oersted at  $450^\circ\text{C}$  and that this was followed by a decrease to zero coercivity at  $700^\circ\text{C}$ , where haematite was formed. Conversely,  $H_c$  for  $\alpha\text{Fe}_2\text{O}_3$  rose on reduction in hydrogen and water vapour to about 300 oersted at about  $350^\circ\text{C}$  reduction temperature, and dropped again to 100 oersted at about  $600^\circ\text{C}$ . Kojima believes that, during the reduction of  $\alpha\text{Fe}_2\text{O}_3$ ,  $\gamma\text{Fe}_2\text{O}_3$  is in fact first formed before  $\text{Fe}_3\text{O}_4$ , and that the coercivity peak is due to this formation of the intermediate  $\gamma$  phase. Further evidence on this important point would be of interest.

A number of experimental investigations of the properties of these oxide powders has been described. Armour (1952) give curves relating the remanent magnetization with previously applied field strength for a number of tape specimens. The form of this remanence curve (cf. also § 2) is important in the applications of recording tapes. Thus a small remanence in low fields is desirable if the tape is to be insensitive to stray fields, for example from neighbouring elements of the tape which may carry a signal. In general the low field 'foot' of the remanence curve extends to fields of the order of the bulk coercive force; it is influenced by variations of the coercive forces of the individual particles of the powder (Wohlfarth 1955c), and these should ideally be kept small for this and other reasons.

Krones (1955) and Müller (1955) have also described the measurement of remanent magnetization curves for various tape specimens which have been under the influence of combined direct and high-frequency alternating fields. These experiments simulate the behaviour of a tape under actual operating conditions which involve the use of the linearizing effect of a high-frequency bias current in the recording head. Under these conditions an optimum current is required for the largest output signal, the corresponding field being of the order of the bulk coercive force. The linearizing action of the bias field, which leads to a reduction of the distortion, may be understood in principle by analogy with the effects of alternating fields during the development of the anhysteretic remanent magnetization (Westmijze 1953, Wohlfarth 1957).

Apart from the magnetic properties of tapes leading to high and distortion-free output signals, the frequency response and basic noise are important tape properties. The first is strongly influenced by the coercive force which should be as high as possible commensurate with the ease of erasing tape signals by alternating current methods. The result of a large amount of investigation of basic tape noise is that the integrated noise is proportional to the mean volume of the powder particles (Howling

1956). An investigation into the effects which the properties of the oxides, such as particle size, the presence of additions, etc., have on the electro-acoustical properties of the tape has been reported by Schrader *et al.* (1953). Greiner (1952) investigated one aspect of the difficult and important problem of particle agglomeration. He found that, if the agglomerates are in the form of chains, the remanence and hence the output signal may be improved. This result could be understood in terms of improved shape anisotropy. Osmond (1952, 1953, 1954) carried out a careful analysis of the magnetic properties, especially the coercive force, of iron oxides used in tape manufacture. The basis of this discussion is the single domain treatment, and Osmond concludes that shape anisotropy is mainly responsible in determining the coercive force of  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{Fe}_2\text{O}_3$  powders. Effects such as crystal anisotropy, particle packing and shape variations and the presence in acicular particles of non-magnetic cavities (cf. Franklin and Campbell 1955, Campbell 1957) were also considered. Effects of the finite thickness of the magnetic component of tapes have been investigated by Nagai and Iwasaki (1959).

#### 4.3. Basic Experiments on Oxide Powders

The above brief discussion of some of the more fundamental investigations on oxide materials used for tapes aims to show which of the properties of the magnetically hard materials are considered as having a technological importance in the application of tapes. Recently more searching basic experiments on the properties of iron oxide powders have been reported.

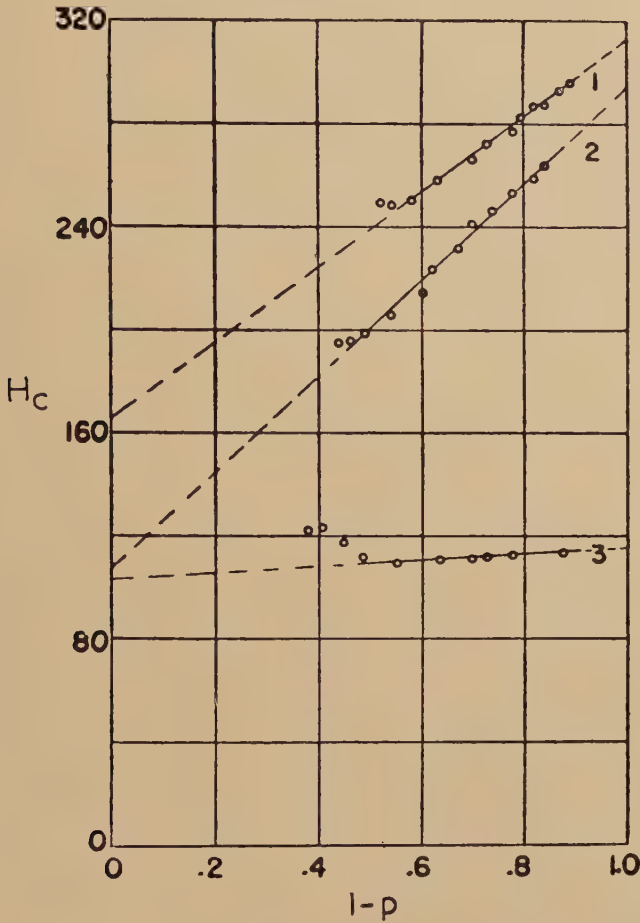
If the properties of the powders are to be interpreted in any sense, values of the anisotropy constant and saturation magnetization are required. For  $\text{Fe}_3\text{O}_4$  single crystals the variation of  $K_1$  with temperature has been measured several times, for example by Bickford (1950), Smith (1956) and Bickford *et al.* (1957), the last also measuring the second order constant  $K_2$  and the large effects on  $K_1$  and  $K_2$  of adding small amounts of cobalt to single crystal magnetite (cf. also § 5). The room temperature value of  $K_1$  is about  $-1.2 \times 10^5 \text{ erg cm}^{-3}$ . On lowering the temperature  $K_1$  increases, passes through zero at about  $130^\circ\text{K}$  and assumes large positive values below the crystallographic transformation temperature, about  $115^\circ\text{K}$ , where the crystal structure becomes orthorhombic. High-frequency measurements on powders by Birks (1950) give  $K_1 = -1.3 \times 10^5$  at room temperature. As single crystals of  $\gamma\text{Fe}_2\text{O}_3$  do not exist, Birks' is the only method and gives  $K_1 = -4.7 \times 10^4 \text{ erg cm}^{-3}$  at room temperature. Extension of this and other methods of measuring the anisotropy constants of  $\gamma\text{Fe}_2\text{O}_3$  at different temperatures would be of great interest.

The saturation magnetization of  $\text{Fe}_3\text{O}_4$  is also well established (see Bozorth 1951 b p. 242, Henry and Salkovitz (1959) give  $p_B = 1.26$  per iron atom). For  $\gamma\text{Fe}_2\text{O}_3$  Henry and Boehm (1956) give for the saturation value  $p_B = 1.18$  per iron atom. The crystal structure of  $\text{Fe}_3\text{O}_4$  both above and below the transformation is well understood (see, for example, Hamilton



1958). For  $\gamma\text{Fe}_2\text{O}_3$  the structure is much more complex than cubic spinel (Braun 1952b, Van Oosterhout and Rooijmans 1958) and seems to be still under discussion.

Fig. 4.2

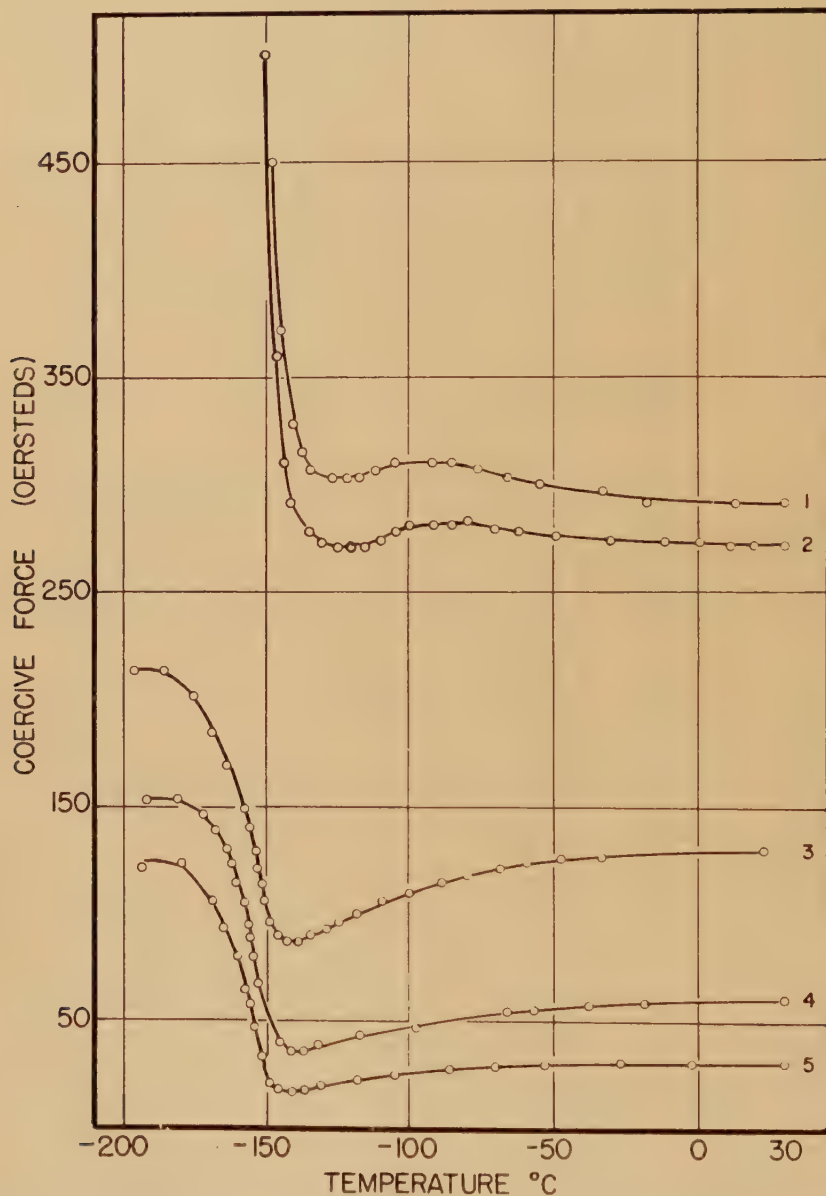


Dependence of coercive force on packing factor.  $H_c$ , coercive force;  $p$ , packing factor. Curves 1, 2, 3 as in text. After Morrish and Yu (1955).

A series of experimental studies on oxide powders has been reported by Morrish and associates. Morrish and Yu (1955) measured the dependence of the coercive force of powders with varying shapes and sizes on their packing factor  $p$ . Figure 4.2 shows this variation for (1) acicular  $\text{Fe}_3\text{O}_4$ , (2) acicular  $\gamma\text{Fe}_2\text{O}_3$ , (3) non-acicular  $\text{Fe}_3\text{O}_4$ . Néel's formula (2.2) is not obeyed in any case, and this was ascribed to one or more of the following effects: Magnetocrystalline anisotropy, which can give a compression independent coercivity about 160 oersted for magnetite; multidomain effects,

which, it is argued, might also lead to a compression independence; and the presence of non-magnetic cavities or inclusions (cf. Osmond 1953). It is also possible that the variation of the packing factor in these experiments may not cause a uniform change of density due to persistent clustering.

Fig. 4.3



Temperature variation of coercive force for  $\text{Fe}_3\text{O}_4$ . For numbers on curves see text. After Morrish and Watt (1958 a).

The possibility that Néel's formula itself is not always reliable was discussed in § 2. Morrish and Watt (1957) reported measurements on  $\gamma\text{Fe}_2\text{O}_3$  particles with mean lengths about  $0.5\mu$  but with varying mean axial ratios  $\bar{m}$ . For four samples 1, 2, 3, 4 with  $\bar{m} = 6.5, 5.5, 5.2$  and  $3.3$ , respectively, an approximately linear dependence of  $H_c$  on  $p$  was obtained for sample 1 and a constant coercivity independent of  $p$  for sample 4. For sample 3,  $H_c$  is constant for  $p < 0.15$  and then varies approximately linearly for higher values of the packing factor. These results were taken to mean that the most acicular particles investigated (sample 1) were single domain and the least acicular (sample 4) multidomain, in agreement with general expectations (Stoner and Wohlfarth 1948, Morrish and Yu 1955). For the intermediate case (sample 3) the critical size increases with increasing compression, in agreement with Kondorsky's (1952 a, b) discussion. Later Morrish and Watt (1958 a) carried out measurements of the temperature dependence of the coercive force of  $\gamma\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  powders over the range  $77^\circ$  to  $300^\circ\text{K}$ . For acicular  $\text{Fe}_3\text{O}_4$  powders with axial ratios 8 (curve 1) and  $6.5$  (curve 2) and lengths about  $0.5\mu$  the results are shown in fig. 4.3. The other curves (3, 4, 5) are for larger irregularly shaped multidomain particles. For these the temperature variation is related to that of the crystal anisotropy which determines the Bloch wall thickness roughly as  $K_1^{-1/2}$ . For the smaller particles (curves 1 and 2) the slight increase of coercivity on lowering the temperature reflects the increase of the shape anisotropy, proportional to the saturation magnetization, and the rapid increase near the transformation temperature the increase of the crystal anisotropy in this range, where both types of anisotropy are about equally effective. Data are also given for the  $\gamma\text{Fe}_2\text{O}_3$  powders 1 and 4 of Morrish and Watt (1957);  $H_c$  was found to increase on lowering the temperature, reaching over 400 oersted for sample 1 at  $77^\circ\text{K}$ . No analysis of the results can be made in the absence of thermal data on crystal anisotropy and saturation magnetization. The fact that the coercivity, temperature curves are monotonic over the range  $77^\circ$  to  $300^\circ\text{K}$  implies that  $\gamma\text{Fe}_2\text{O}_3$  suffers no crystallographic transformations in this range (see also Blackman *et al.* 1957). Morrish and Watt (1958 b) have also reported compression and thermal measurements on an  $\text{Fe}_3\text{O}_4$  powder and a  $\gamma\text{Fe}_2\text{O}_3$  powder prepared from it by oxidation at  $300^\circ\text{C}$  for 2 hours, both specimens having a mean length  $0.6\mu$  and mean axial ratio  $5.2$ . By reference to their earlier papers, discussed above, Morrish and Watt conclude that the magnetite particles are in the main multidomain and the  $\gamma\text{Fe}_2\text{O}_3$  particles single domain, in agreement with the calculations of Morrish and Yu (1955).

A different type of investigation on acicular  $\gamma\text{Fe}_2\text{O}_3$  powders has been described by Johnson and Brown (1958 a). By a mathematical analysis of curves relating the remanent magnetization attained after partial a.c. demagnetization they were able to determine the extent of the shape variations of their particles. The calculated shape distribution curve had a maximum at an axial ratio  $1.6$ , which is in agreement with the observed



coercive force, about 300 oersted, but is much lower than the value, about 5, obtained by direct electron microscope observation. As this disagreement might be partly ascribed to particle interactions Johnson and Brown (1958 b) investigated the effect of diluting the powders down to various concentrations ranging to 0.1%. There is only a slight shift of the peak of the shape distribution curve towards higher axial ratios for the higher degrees of dilution. Although steps were taken to prevent clustering by ball milling, this may well not have been entirely effective, with relatively more serious results for the more dilute powders. In the same paper Johnson and Brown also investigated various modes by which the remanent magnetization may be acquired (Wohlfarth 1958). The simple relations which exist between these modes under ideal conditions were not observed, due perhaps to particle interactions, incoherent magnetization changes, etc. (cf. § 2). Johnson and Brown (1959 a) extended their method to acicular and non-acicular magnetite powders, investigated at various temperatures. The shape distribution curves were found to change little with temperature, indicating that magnetocrystalline anisotropy has only a small influence.

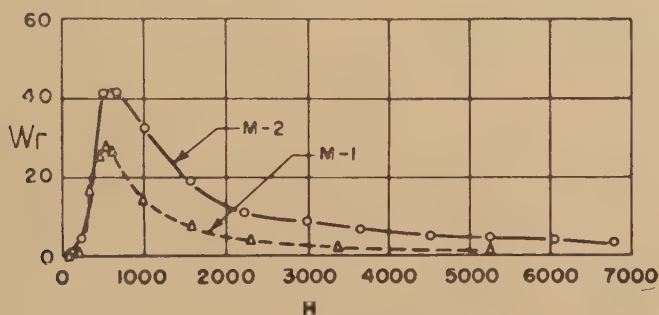
Another investigation on oxide powders ( $\text{Fe}_3\text{O}_4$  and  $\text{Fe} + \text{Fe}_3\text{O}_4$ ) has been reported by Campbell *et al.* (1957). They measured the coercive force and remanence and, using the results of electron microscope counts and approximate theoretical criteria, established the relative volumes of superparamagnetic, single domain and multidomain particles in each sample. The estimated coercivity and remanence agree reasonably well with observation in some but not all cases. For two  $\text{Fe}_3\text{O}_4$  powders the coercivities at room temperature were 320 oersted and the reduced remanences 0.4, although the relative volumes of single domain particles had been estimated as 75% and 3% for the two samples. Campbell *et al.* also measured the rotational hysteresis of the powders, and fig. 4.4 shows the results for the two magnetite specimens referred to above. The data show that some quite hard particles, having critical fields well over 2000 oersteds, were apparently present in the powder ( $2\pi I_0$  for  $\text{Fe}_3\text{O}_4$  is about 3000 oersted). Measurements were also made of the temperature variation of coercivity and remanence. Below the crystallographic transformation temperature a field, applied during cooling, causes a considerable increase of the remanence in the field direction, due to the establishment of strong uniaxial anisotropy of the orthorhombic particles (see also Williams *et al.* 1953).

An interesting experiment on *single* magnetite and  $\gamma\text{Fe}_2\text{O}_3$  particles has been described by Morrish and Yu (1956), using a  $0.5\mu$  quartz fibre torsion balance (Yu and Morrish 1956) which enabled  $1\mu$  size particles to be examined. It was found that for a  $\gamma\text{Fe}_2\text{O}_3$  particle, believed from previous measurements to be single domain, the remanent magnetization after saturation and subsequent application and removal of a reverse field  $H$  changes discontinuously from one state of saturation to the other when  $H$  equals about 800 oersted. For larger or non-acicular

$\text{Fe}_3\text{O}_4$  particles the remanence curve is continuous. These experiments clearly demonstrate the single and multidomain character of small particles, and it would be of great interest to have them extended in obvious ways.

Whereas the coercivities of  $\text{Fe}_3\text{O}_4$  powders have never been observed to exceed a few hundred oersted, Jacobs (1959, and private communications which are gratefully acknowledged) has prepared powders of  $\text{Co}_x\text{Mn}_{3-x}\text{O}_4$  with immensely high coercivities at low temperatures. Observations were carried out at  $4^\circ\text{K}$  after saturation in pulsed fields  $1.4 \times 10^5$  oersted on powders of a few microns size. For the compound with  $x=0$ ,  $H_c = 1.6 \times 10^4$  oersted, with  $x=0.5$  the coercivity has the same value although the saturation magnetization is less, and with  $x=0.95$ ,  $H_c = 2.4 \times 10^4$  oersted, only slightly less than Van Uitert's value for a mixed barium ferrite (1957, cf. § 5). The causes for these high values are still uncertain, although strain effects are suspected to play a part, due, perhaps, to deviations from cubic crystal structure; high crystal anisotropy could also contribute.

Fig. 4.4

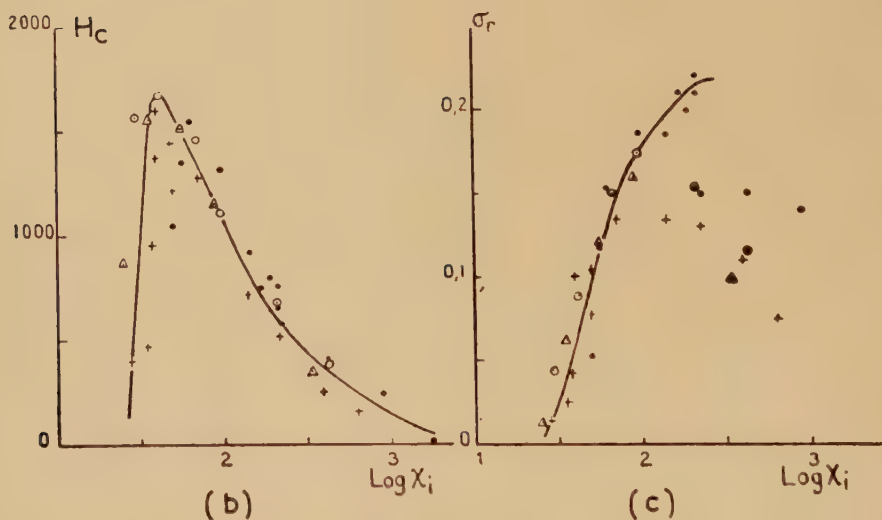
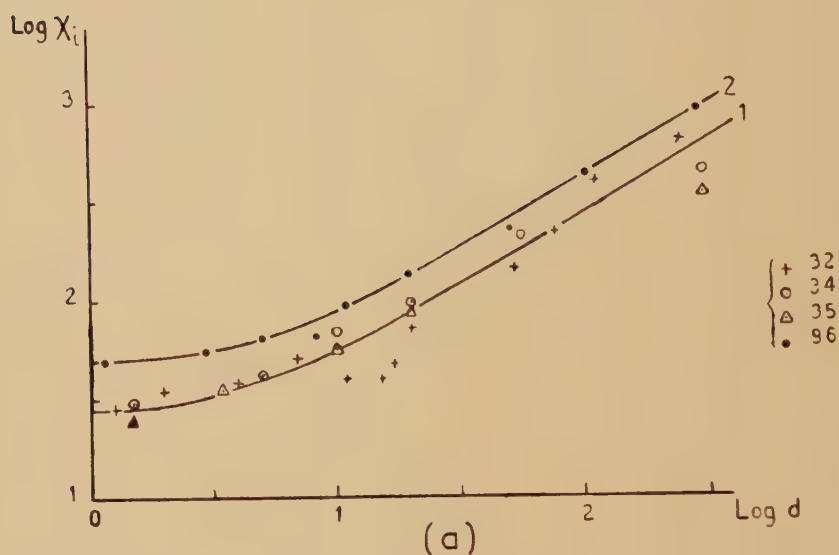


Rotational hysteresis for two magnetite powders.  $W_r$ , rotational hysteresis in dyne-cm  $\text{cm}^{-3} \times 10^{-4}$ ;  $H$ , applied field. After Campbell *et al.* (1957).

#### 4.4. Properties of Haematite and Related Substances

Haematite and related substances, such as haematite-ilmenite solid solutions, are important constituents of rocks. Much of the work on these fascinating materials, carried out before 1951, has been summarized by Chevallier (1951), and the more geomagnetic aspects by Thellier (1951). By that time it was established that haematite is a weakly ferromagnetic substance with saturation magnetization (moment per unit volume) very roughly 2–3 gauss and with a considerable magnetic hardness. The coercivity and initial susceptibility of  $\gamma\text{Fe}_2\text{O}_3$  powders depend on their previous history such as origin (natural or synthetic), method of preparation, particle shape and, ultimately the most important, particle size. Chevallier and Mathieu (1937, 1943) investigated powders with grain size between 1 and  $300\mu$  and coercivities up to 1800 oersted. A selection of their results is given in fig. 4.5; in (a) curve 1 is for natural and 2 for synthetic powders.

Fig. 4.5



Properties of haematite powders. (a) Variation of initial susceptibility  $\chi_i$  with grain size  $d(\mu)$ . (b) Variation of coercivity  $H_c$  (oersted) with  $\chi_i$ . (c) Variation of remanent magnetization  $\sigma_r$  (e.m.u.) with  $\chi_i$ . After Chevallier and Mathieu (1943).



The dependence of coercivity on grain size is seen to be similar to that for other materials, and the general interpretation of the results is presumably the same here as elsewhere. For haematite the maximum coercive force corresponds to a particle size about  $5\mu$ .

Further measurements on the isothermal remanence of haematite powders has been reported by Roquet (1947, see also Thellier 1951). She measured not only the remanence curve but also the curve obtained after partial d.c. demagnetization of the remanence, thus obtaining a value of the remanence coercivity  $H_R$ . For one specimen investigated  $H_R$  was as much as 7600 oersted; the large ratio of  $H_R$  to the normal coercive force  $H_c$ , roughly 4 for this specimen, arises as a result of heterogeneities of the powder which could result from size variations or other causes (cf. Wohlfarth 1958). Other remanence measurements include those of Haigh (1957 a, b) and Rimbert (1956, 1957).

Apart from the Curie point of haematite ( $950^\circ\text{K}$ ) an important magnetic transformation takes place at about  $250^\circ\text{K}$ . Morin (1950, cf. also Honda and Soné 1914, Charlesworth and Long 1939) measured the mass susceptibility of powdered haematite, and found that it dropped from a value constant at about  $130 \times 10^{-6}$  above this temperature to about  $20 \times 10^{-6}$  below it. This last value is close to the paramagnetic susceptibility of haematite, and it hence seemed that the weak ferromagnetism disappears below the Morin transition. Morin also found that the addition of 1% Ti suppressed this transition, but Haigh (1957 a) found that adding up to 10% Ti or Al to a different haematite specimen did not suppress it, but merely shifted the transition temperature to lower values. On the other hand, the transition did not occur in a Triassic sandstone containing haematite plus about 5% Ti. It appears that different specimens of this material can differ profoundly in their structure and properties.

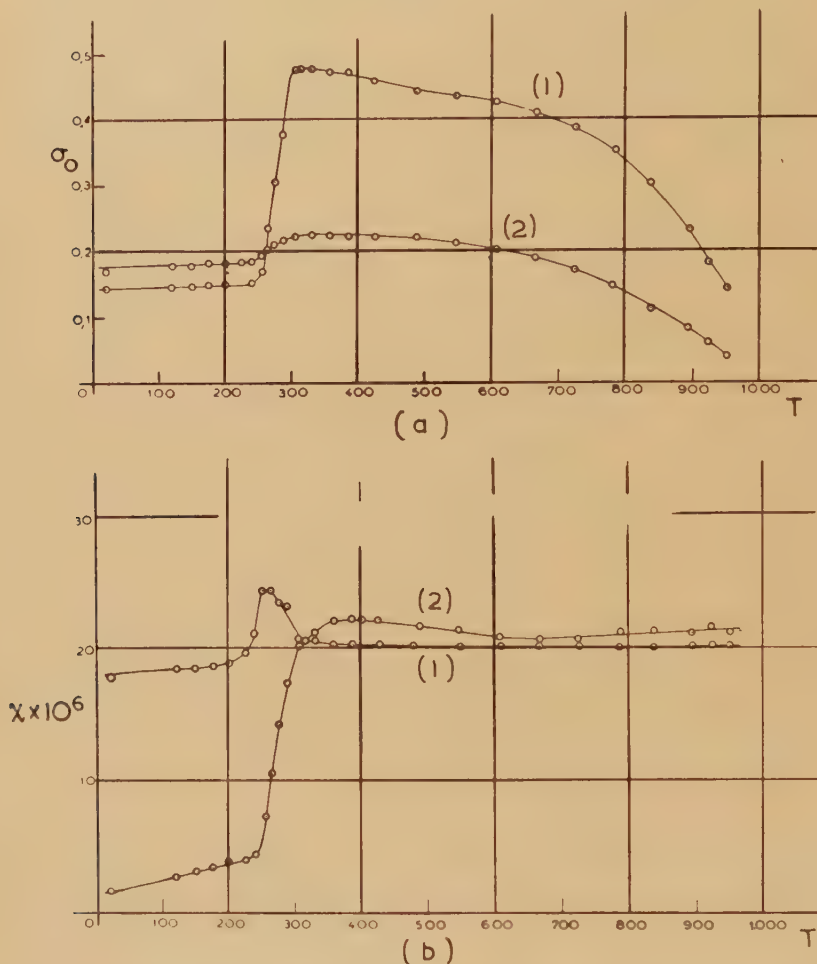
Other experiments on the magnetic properties of haematite near the Morin transition have been reported by Néel and Pauthenet (1952, cf. also Néel 1953 b). They investigated a natural single crystal and found that, the magnetization being represented by the formula

$$\sigma(T, H) = \sigma_0(T) + \chi(T)H, \quad . \quad . \quad . \quad . \quad (4.1)$$

$\sigma_0$  and  $\chi$  varied with temperature  $T$  as shown in fig. 4.6. The mass susceptibility  $\chi(T)$  is anisotropic below the transition but isotropic and equal to  $20 \times 10^{-6}$  above it and the Curie temperature. The weak ferromagnetic moment  $\sigma_0(T)$  may be written as the sum of two parts:  $\sigma_i + \sigma_a$ . Here  $\sigma_i$  is an isotropic component and  $\sigma_a$  an anisotropic one which vanishes below the transition temperature (thus clarifying Morin's original results), but appears, with an anisotropy in the basal crystal plane, above it (Néel 1953 b); both  $\sigma_i$  and  $\sigma_a$  vanish together at the Curie point. The magnetic hardness of haematite may, if this is the correct interpretation of Pauthenet's results, be ascribed to  $\sigma_a$ ; on the other hand there is evidence (see below) that  $\sigma_i$  is itself not perfectly 'soft'. The fact that  $\sigma_a$  does not appear, at least in moderate fields, in the direction of the trigonal axis

implies that there is a strong negative crystalline anisotropy constraining the magnetization to lie in the 'easy' plane and changing drastically at the Morin transition. Evidence on the magnitude of this anisotropy is summarized below; the nature and magnitude of the planar anisotropy is still uncertain. Recent work by Lin (1959) throws some doubt on the above interpretation.

Fig. 4.6

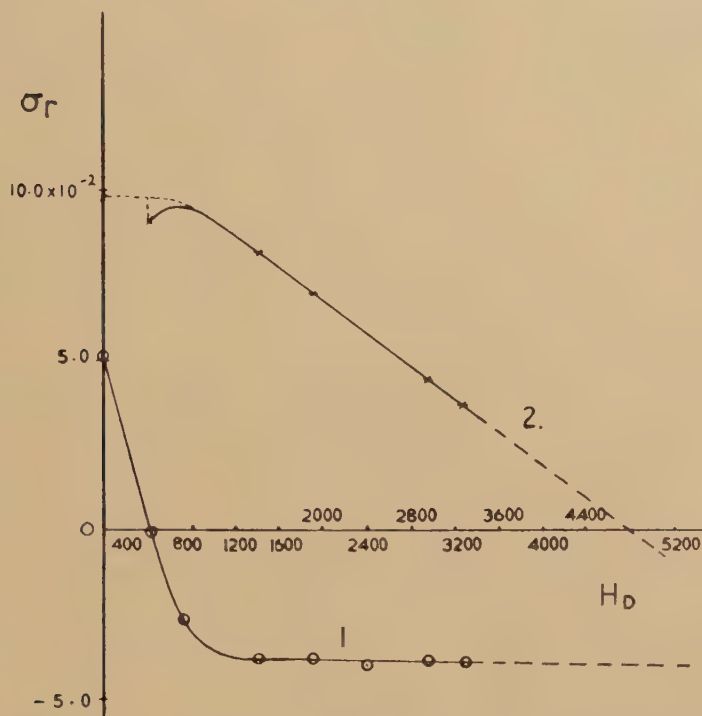


Magnetization of a haematite crystal. Variation of (a)  $\sigma_0(T)$  and (b)  $\chi(T)$  with temperature  $T^{\circ}\text{K}$  (1) in the basal crystal plane, (2) parallel to the trigonal axis; see eqn. (4.1). After Néel and Pauthenet (1952).

Other related observations on the Morin transition have been reported by Guillaud (1951 a), Bizette *et al.* (1953), and, in particular, by Haigh (1957 b). He used synthetic haematite powders dispersed in Plaster of Paris. On cooling below 250  $^{\circ}\text{K}$  and then reheating above the transformation, it was found that a very large decrease of the remanence had occurred

compared to the value observed before the temperature cycling; this thermal hysteresis does not occur if the cycling takes place in a strong magnetic field (cf. also Lin 1959). Another experiment aimed at separating the isotropic and anisotropic components of  $\sigma_0$  (cf. eqn. (4.1)),  $\sigma_i$  and  $\sigma_a$ . This was done by measuring the d.c. demagnetization of the remanence as a function of field strength both above the Morin transition, where both components occur, and below it, where  $\sigma_i$  retains its high temperature

Fig. 4.7



D.C. demagnetization curves of haematite powders. Curve 1, isotropic component of magnetization; curve 2, anisotropic component.  $\sigma_r$ , remanent magnetization after demagnetization in field  $H_D$ , oersted. After Haigh (1957 b).

value, but  $\sigma_a = 0$ . The observed curves are shown in fig. 4.7, where the analysis into these two components has been carried out. The remanence coercivity  $H_R$  for the  $\sigma_A$  component is 4800 oersted, but the  $\sigma_i$  component, with  $H_R = 430$  oersted, is by no means magnetically soft. The resultant  $H_R$ , 3200 oersted, is less than half Roquet's value (1947). The ordinary coercive force of this powder is, from fig. 4.7, about 1000 oersted, and the large ratio  $H_R/H_c$  is again to be ascribed to heterogeneities. Haigh also measured the temperature variation of the remanence coercivity above and below the Morin transition, and found a very sharp decrease at this temperature. He concludes from measurements on a range of powder specimens that there is a great variability in their properties.



Another way by which the Morin transition may be observed is by investigating electron shadow patterns at various temperatures (Blackman *et al.* 1957). The leakage field, originating from a single crystal, causes the pattern to assume a characteristic cycloidal shape above the transition, but this disappears very sharply below it, due, presumably, to the disappearance of the anisotropic component of magnetization. The results for two temperatures are shown in fig. 4.8. (Pl. 3).

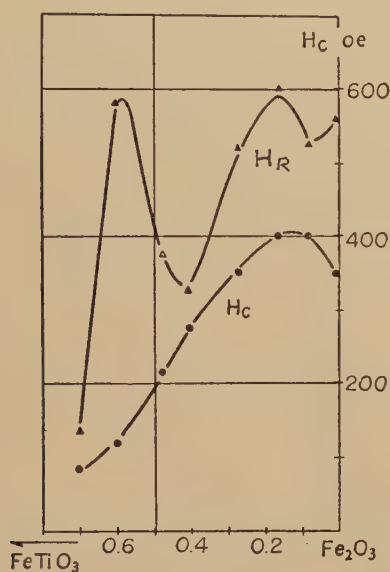
As pointed out above, the anisotropic component of magnetization of a crystal of haematite is constrained to lie in the basal crystal plane by a very strong magnetocrystalline anisotropy. This has been investigated by ferromagnetic resonance methods by Anderson *et al.* (1954). The anisotropy field was found to be as large as  $3 \times 10^4$  oersted, the anisotropy in the basal plane 6-fold and weak, and all traces of resonance to disappear below the transition temperature. Later Kumagai *et al.* (1955) and Y. Kojima (1955, cf. also Shimizu 1956) reported resonance results which seem to differ to some extent from Anderson's. Kojima found the symmetry of the anisotropy in the basal plane to be 2-fold, while Kumagai could detect no symmetry there at all, obtained for the anisotropy field characteristic of the trigonal axis a value of  $4 \times 10^4$  oersted, and found that the resonance only disappears at  $220^\circ\text{K}$ .

A full discussion of the origins of the weak ferromagnetism of haematite is beyond the present scope. The question whether it is a fundamental or a secondary phenomenon has not yet received a satisfactory answer. Néel (1949c) ascribed the phenomenon to magnetite impurities in an epitaxial relationship with the haematite lattice. A related interpretation is in terms of small deviations from stoichiometry (Néel 1953b), leading to a slight ferrimagnetic moment above the fundamental antiferromagnetism. A tentative suggestion that the source of ferromagnetism lies in the antiferromagnetic domain walls (Néel 1955b) was examined further by Li (1956), who believed that these walls are stabilized above the Morin transition by lattice defects, while this is impossible below it due to the overriding effect of the crystal anisotropy. Jacobs and Bean (1958) have also discussed this possibility as well as another one, that an exchange anisotropy (cf. §3) exists between the antiferromagnetic  $\alpha\text{Fe}_2\text{O}_3$  and Finch and Sinha's (1957) ferrimagnetic  $\beta\text{Fe}_2\text{O}_3$  phases. Dzyaloshinsky (1958) has ascribed the phenomenon to relativistic spin-lattice and magnetic dipole interactions, but Bertaut (1958) has shown that dipole interactions can not account for the observed behaviour.

Whatever the origin of the weak ferromagnetism of haematite, the hysteretic properties of powders are most likely explicable in terms of single domain effects, since the critical size is here probably quite large. The governing anisotropy must be magnetocrystalline since the saturation magnetization is small. The most significant experimental fact is that different haematite specimens can differ greatly in their magnetic properties; this would imply that secondary causes are responsible for the ferromagnetism.

Apart from haematite, magnetic hardness is also developed in other rhombohedral powder materials. Among these there is great geophysical interest in haematite-ilmenite solid solutions,  $\alpha\text{Fe}_2\text{O}_3\text{--FeTiO}_3$  (see, for example, Nicholls 1955). These materials have been studied by Chevallier *et al.* (1955), and in particular by Nagata and associates. Akimoto (1955) measured the field and temperature dependence of the magnetization, and Nagata and Akimoto (1956) determined the dependence of the coercive force of synthetic and natural powders on the ilmenite content  $x$ . For the specimens investigated (size  $5\text{--}15\ \mu$ ) large coercive force (up to 900 oersted) was observed for  $x < 0.55$  where the magnetization is low, and low coercivity for  $0.55 < x < 0.75$  where it is higher by factors  $\sim 50$ . The probable cause

Fig. 4.9



Coercive force of haematite-ilmenite powders. After Uyeda (1958).

of the magnetic hardness of the haematite-rich powders is thus their crystal anisotropy. The saturation magnetization of a specimen with  $x=0.5$  may be increased (Ishikawa and Akimoto 1957a) by slow cooling from below  $1100^\circ\text{C}$ , due to a partial ordering process. The dependence on ilmenite content  $x$  and heat treatment of the magnetization has been further investigated by Ishikawa and Akimoto (1957b), Bozorth *et al.* (1957) and Bozorth and Kramer (1959). Uyeda (1957) investigated the corresponding coercive forces in greater detail. Figure 4.9 shows the room temperature variation with ilmenite content of the coercivity  $H_c$  and remanence coercivity  $H_R$ ; the results are difficult to interpret. Uyeda also measured the temperature variation of the coercivity and also of the

thermoremanent magnetization which is roughly proportional to  $H_c$  (cf. Néel 1955 a). Uyeda (1958—a comprehensive review) believes that some of the complex properties of the haematite-ilmenite series may be explicable in terms of exchange anisotropy effects (cf. § 3), the interactions being between the ferrimagnetic, weakly ferromagnetic and antiferromagnetic phases present in this system.

Brief reference should be made to another class of magnetically hard rhombohedral powder materials, namely the substances  $\text{CoMnO}_3$  and  $\text{NiMnO}_3$  (Swoboda *et al.* 1958). For fine powder compacts of these materials coercive forces as high as  $9 \times 10^3$  oersted were obtained for the cobalt compound and 1240 oersted for the nickel compound, with an indication that particle size reduction by cold working leads to a coercivity increase. The reduced remanent magnetization of a random particle assembly was found to be high, about 0.7, indicating, as in haematite, a non-uniaxial anisotropy with some symmetry in the basal crystal plane. The difference between these materials and haematite is that the saturation magnetization is high, about 80 gauss at room temperature, implying that the magneto-crystalline anisotropy to produce the high observed coercivities must also be high. Further evidence for these conclusions is provided by the ferromagnetic resonance investigations of Jarrett and Waring (1958). The temperature variation of the magnetization has been measured by Bozorth and Walsh (1958) and by Bertaut and Forrat (1958), who also investigated the crystal structure (see also Bozorth and Kramer 1959, Cloud 1958).

## § 5. MAGNETICALLY HARD FERRITES

Although ferrite materials are usually discussed in connection with soft magnetic substances, there are two broad groups of substances which exhibit pronounced magnetic hardness and have been used for permanent magnet applications. These are the cobalt and the barium ferrites and materials closely related to them. Fuller details than are possible here are given in the book of Smit and Wijn (1959).

### 5.1. Cobalt Ferrites; Powders and Sintered Materials

Kato and Takei discovered in 1933 that if equal quantities of powdered cobalt ferrite ( $\text{CoO} \cdot \text{Fe}_2\text{O}_3$ ) and magnetite are mixed and compressed, sintered at  $1000^\circ\text{C}$  and then magnetically annealed by cooling in a magnetic field from  $300^\circ\text{C}$  to room temperature, a permanent magnet material is obtained with remanent induction 3 to  $5 \times 10^3$  gauss and coercive force 400 to 600 oersted. The magnetic annealing treatment produces a material with anisotropic magnetic properties, and this material has been produced commercially under the names Vectolite and Caslox I. Coercive forces of the same order as Kato's were also obtained by Jellinghaus (1936 a), who failed, however, to attain the Japanese remanence values. Some improvement of the maximum energy product



of sintered cobalt ferrite magnets was achieved by Takei and Sugimoto (1955). They found that, on adding up to 1% of the oxides  $\text{As}_2\text{O}_3$  or  $\text{Bi}_2\text{O}_3$ , the value of  $(\text{BH})_{\text{max}}$  may be raised by as much as 30%. The additions improve the degree of sintering and so raise the remanence and slightly lower the coercive force.

A different method of preparation of oxide magnet materials has been described by Société d'Ugine (1948a). Chemical methods were used, rather similar to those used for the preparation of metallic powder magnets (cf. § 3). These involved the precipitation from a solution of organic iron and cobalt salts, the salts being then oxidized below  $600^\circ\text{C}$  and compacted. The oxides may be further heated with or without a magnetic field. Typical results for a compacted bar with ratio of iron to cobalt content equal to 2 and density 3.8 are as follows: Coercivity after oxidation and compacting 2100 oersted, after re-heating at  $460^\circ\text{C}$  and slow cooling 4200 oersted, which was unchanged by carrying out the treatment in a magnetic field. The remanent magnetization, however, was found to be 50% higher in the magnetic annealing, i.e. the preferred direction. The Fe/Co ratio about 2 seems to be the optimum value, both remanence and coercive force decreasing for values of the ratio much different from this. The coercive forces of the magnets produced by these chemical methods are much higher than those produced by the mechanical methods of Kato and Takei. This difference is doubtless due to differences in particle size. The high values of the coercive force of the Ugine and later ferrite powders are presumably mainly a result of strain or magnetocrystalline anisotropy effects in the powder particles, whose saturation magnetization is rather low. These effects could conceivably arise as a result of deviations from cubical crystal structure (Goodenough and Loeb 1955, Dunitz and Orgel 1957, Wojtowicz 1959 and other references outside the present scope), but this has not yet been established. An analogy is suspected with other non-cubic materials, such as tetragonal CoPt (see §§ 3 and 8). The high positive magnetocrystalline anisotropy of cobalt ferrites has also sometimes been ascribed to the properties of the cobalt ions themselves in the presence of their crystalline environments (see Van Vleck 1959, Slonczewski 1958a, b).

A comprehensive programme of research on cobalt ferrites has been carried out by Guillaud and associates. He first (Guillaud *et al.* 1950, Guillaud 1951 b) investigated materials similar in composition to Vectolite. Measurements of the coercive force at different temperatures gave the following results: Room temperature, up to  $3 \times 10^3$  oersted;  $77^\circ\text{K}$ , up to  $9 \times 10^3$  oersted;  $20^\circ\text{K}$ , up to  $1.7 \times 10^4$  oersted. An inverse relation was established between coercivity and saturation magnetization, but from the observed magnetostriction values it was concluded that strain anisotropy is not in the main responsible for this magnetic hardness, which is ascribed to the crystal anisotropy of the powders.

A further series of investigations has been reported by Guillaud (1953) on the substances  $(\text{CoO})_{1-x} \cdot (\text{Fe}_2\text{O}_3)_x$ , with  $x$  between 0.5 and 0.6, which

had been prepared by sintering. The magnetic properties of specimens with density less than about 3 are ascribed to rotational magnetization changes, and of those with a higher density increasingly to boundary motion effects, with a gradual coercivity decrease. It is believed that boundary motion is inhibited for the more porous specimens, the boundaries being envisaged as anchored to the non-magnetic cavities. These cavities in the sintered ferrite are regarded as magnetically equivalent to particles in an otherwise non-magnetic medium, and the theoretical results of § 2 are then applicable. The magnetostriction coefficients, measured either by x-ray (Guillaud and Sage 1953) or mechanical (Vautier 1954) methods, are large and negative for the non-oriented specimens and also for those specimens which have been magnetically annealed, the large values here occurring in a direction perpendicular to the direction of orientation. The observed coercive forces of these ferrites are ascribed to uniaxial strain anisotropies, at least at temperatures above about 200°K. For a particular specimen, investigated at different temperatures in a range where the magnetostriction constant  $\lambda$  varies strongly, the coercive force was found to be proportional to  $\lambda$ . For a range of values of the composition  $x$  this proportionality no longer holds, due, it is believed, to variations of the internal stresses with iron content. At temperatures below 200°K the coercivity is no longer determined by strain anisotropy alone, and here magnetocrystalline anisotropy is believed to have an effect. Guillaud (1953) also reports results on the remanence, the initial susceptibility and the energy of magnetization, and these seem to confirm the above tentative explanation of the magnetic hardness in the sintered cobalt ferrites.

Magnetostriction measurements on magnetically annealed cobalt ferrites have also been reported by Weil (1952), Bozorth, Tilden and Williams (1955), Wijn *et al.* (1957) and others, and very large values have been observed.

The experiments described by Guillaud (1953) were stated to be on single phase materials, the heterogeneity responsible for magnetic hardness residing in the pores of the sintered materials. Some x-ray diffraction measurements on Vectolite by Geisler (1951a; see also discussion on Guillaud's 1953 paper) showed, however, that here a second phase precipitates after ageing at or below 800°C. The precipitate has the rhombohedral structure of  $\alpha\text{-Fe}_2\text{O}_3$ , but evidence was found that in the early stages of ageing it has cubic spinel structure coherent with the matrix, and with a lattice discrepancy about 0.7%. Magnetic hardness was then attributed to coherency strains.

Other experiments on cobalt ferrite powders have been reported by Berkowitz and Schuele (1959), who produced their specimens by the low temperature treatment of the coprecipitated metal oxalates. For particles in the size range 0.03 to 0.07  $\mu$  single domain behaviour was suspected, with coercivity up to 2000 oersted at room temperature, and a reduced remanence close to 0.5. From the magnitude and temperature dependence

of the coercivity it was concluded that this is determined by the magneto-crystalline anisotropy. For particles outside the above size range remanence and coercivity were found to drop in the usual way. Berkowitz and Schuele also investigated copper and nickel ferrite powders which had a lower maximum coercivity.

Lotgering (1956) prepared sintered  $\text{FeCo}_2\text{O}_4$  material, and observed a high coercive force ( $1.3 \times 10^4$  oersted) at  $77^\circ\text{K}$  but a very low one (79 oersted) at room temperature. It may be significant that this material is 2-phase under certain conditions of heat treatment, although the crystal structure is always spinel.

### 5.2. Cobalt Ferrites; Magnetic Annealing

The mechanism of the heat treatment of cobalt ferrites in a magnetic field has been investigated by Williams *et al.* (1956). As in Nesbitt's work on permanent magnet alloys (§7) the method used involved the measurement of torque curves; precipitation was detected from electron diffraction patterns. The measurements were performed on cobalt as well as on cobalt-zinc ferrites. The torque curves of those ferrites which respond to the annealing treatment show a reversal in sign as the measuring field increases, showing that at low fields the shape anisotropy of precipitated particles is dominant and at high fields the intrinsic crystal anisotropy. The precipitates were found to be very small (a few hundred A.U. in size), to be oriented close to the direction of the annealing field and to have a spinel structure with about the same lattice constant as the matrix. The precipitates formed during heat treatment in the absence of a field are randomly oriented. Some of the ferrite specimens do not respond to magnetic annealing, and these show neither torque reversals nor electron diffraction evidence of precipitation. The evidence from these measurements is, therefore, that anisotropic magnetic hardness is attained in the same way in cobalt ferrites as in permanent magnet alloys of the Alnico type (§7), i.e. by the preferential nucleation and growth of precipitate particles with shape anisotropy. These results have been verified by the neutron diffraction observations of Prince (1956).

The situation is, however, still far from clear. Iida *et al.* (1955, 1958) investigated cobalt ferrites with  $\text{Co}/(\text{Fe} + \text{Co})$  ranging from 0 to 0.42. The specimens were prepared by annealing in oxygen gas followed by slow cooling, after which the magnetic annealing treatment was performed in several ways. The pressure of the oxygen gas during this treatment was controlled, and was found to have a profound influence on the uniaxial anisotropy induced by the magnetic field: the anisotropy increases steadily as the degree of oxidation increases. From this and other results Iida concluded that the uniaxial anisotropy in these ferrites is due to the effects of directional short range order among the magnetic ions and cobalt cation vacancies in the spinel matrix (Néel 1954 b).

Wijn *et al.* (1957) measured the induced uniaxial anisotropy and other properties of the sintered ferrites  $\text{Co}_x\text{Fe}_{1-x}^{2+}\text{Fe}_2^{3+}\text{O}_4$ , with  $x$  between 0 and 0.8. For these materials it was observed that the minor hysteresis



loops are in many cases constricted, the major loops being normal. If the specimens are magnetically annealed then both major and minor loops take up an extremely rectangular shape. The magnitude and direction of the anisotropy was also measured. The anisotropy constant was found to reach a maximum value  $1.2 \times 10^6 \text{ erg cm}^{-3}$  at a composition  $x=0.4$ . The direction of the uniaxial anisotropy was found to be not necessarily parallel to that of the inducing field, but to the nearest crystallographic axis. The absence of a second phase and the temperature variation of the hysteresis loop shapes led Wijn to conclude that the uniaxial anisotropy arises as a result of directional ordering, as in the Japanese work described above. This ordering also influences the domain walls and thus causes the loop constrictions. Similar results for cobalt-containing ferrites have also been reported by Kornetzki *et al.* (1955a, b), Eckert (1957) and v. Kienlin (1958); the last concludes also that directional ordering effects are at play in these materials.

Penoyer and Bickford (1957) have reported experiments on the effect of magnetic annealing on the properties of single crystals of cobalt ferrites  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ , with  $x$  up to 0.15. If  $\theta_A$  is the angle between the [100] axis and the annealing field, then it was found that  $\theta_C$ , the angle between [100] and the uniaxial preferred direction, is not equal to  $\theta_A$ , the difference  $(\theta_A - \theta_U)$  and the uniaxial anisotropy constant  $K_U$  being both strongly dependent on the angle  $\theta_A$ . These results differ from those of Bozorth *et al.* (1955). The detailed results of Bickford were found to be incompatible both with a precipitate model of magnetic annealing and with one involving directional ordering. A new model was therefore proposed, which involves the effect of cation vacancies on the movement of cobalt ions between equivalent cation sites (Bickford *et al.* 1958, Slonczewski 1958a, b, 1959). Fuller discussion of this problem is outside the scope of this article, but it seems at present as though it is the cobalt ions themselves which are responsible for the properties of these materials, the precipitate model being less likely to be relevant here than in permanent magnet alloys. In order to resurrect this model it is necessary to have more evidence as to the nature and properties of the precipitates.

Foner and Artman (1958) have measured the magnetization along different crystallographic directions, the cubic and uniaxial anisotropy coefficients and the remanent magnetization of a single crystal of cobalt ferrite magnetically annealed in a field  $8 \times 10^3$  oersted parallel to the [100] direction. From the data it was concluded that along this direction magnetization proceeds by the movement of  $180^\circ$  walls, along [010] and [001] initially by rotation and then, beyond a critical field about  $3 \times 10^3$  oersted, by a more complex process, and along [011] by an even more complex series of processes. Foner and Artman ascribe the torque reversals observed by Williams, Heidenreich and Nesbitt (1956) to this particular combination of magnetization changes. From the magnetization curves also they deduce the values of the cubic and uniaxial anisotropy coefficients,  $K_C$  and  $K_U$ . These were found to be strongly temperature

dependent, as shown in table 5.1. The large low temperature values give rise to pronounced hysteresis behaviour in this range, for example, a loop area over  $10^7$  gauss-oersted at  $4.2^\circ\text{K}$ . Foner and Artman proposed that the uniaxial anisotropy of cobalt ferrite is a result of internal stresses produced by precipitate particles which are oriented, the stresses combining with the large magnetostriction coefficients to produce high  $K_U$  values. The precipitates are suspected to be  $\alpha\text{Fe}_2\text{O}_3$ , as with Geisler (1951 a), with whose interpretation the present one has points in common (the presence of haematite precipitates has also been suspected by others). Artman and Foner (1959) later gave a mathematical analysis of the problem of magnetization changes in the presence of mixed anisotropies of the type observed in their experiments.

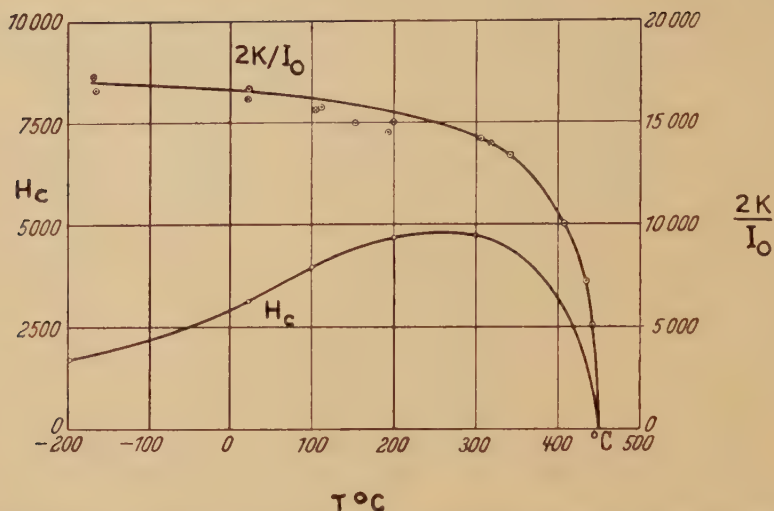
Table 5.1. Cubic and uniaxial anisotropy coefficients of cobalt ferrite.  
After Foner and Artman (1958)

$T^\circ\text{K}$	$K_C \times 10^{-6} \text{ erg cm}^{-3}$	$K_U \times 10^{-6} \text{ erg cm}^{-3}$
300	3.0	0.52
77	18.0	3.3
4.2	19.0	8.9

### 5.3. Barium Ferrite

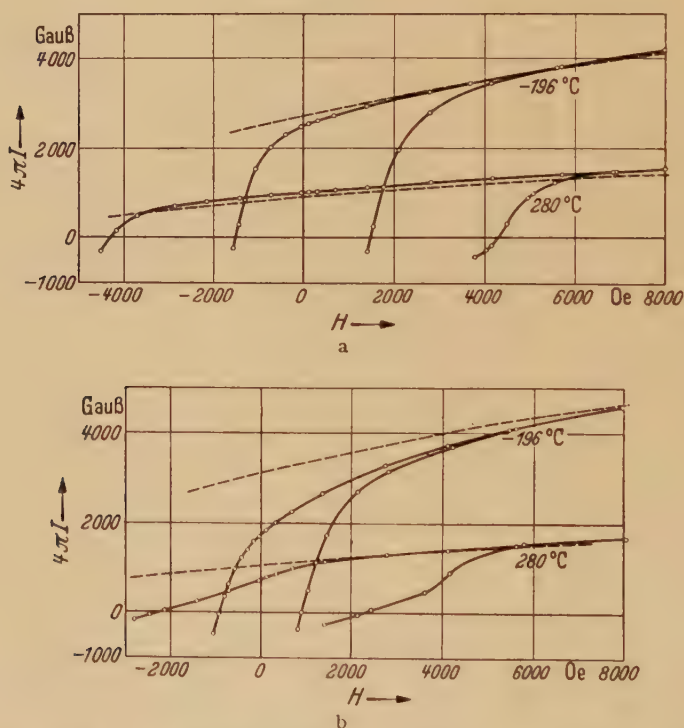
Ferrite materials with hexagonal crystal structure include as the prototype the barium ferrite  $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ , which was first developed by Went *et al.* (1952) as the sintered permanent magnet material Ferroxdure (other trade names have also been used). Although the material consists of sintered powder particles with a relatively large critical size (about  $1.3\mu$  at room temperature, according to Went *et al.*), experimental investigations on its structure and properties show that the magnetization processes are not in general purely rotational, but that domain wall motion effects are usually of great importance. If this were not so then the coercive force for a barium ferrite magnet with small crystallites, governed in its magnetic properties by the uniaxial crystal anisotropy constant  $K$ , which arises from the hexagonal crystal structure, should be determined by the factor  $2K/I_0$ , where  $I_0$  is the saturation magnetization. Went *et al.* measured both  $K$  and  $I_0$  over a wide temperature range, and fig. 5.1 compares  $2K/I_0$  with the coercive force of a material with small crystallites of size about  $1\mu$ . The deviations between the observed and ideal coercive forces are very pronounced, showing the importance of wall motion effects in influencing the observed values. For magnets with coarser grained crystallites this effect is even more important, and the coercive forces are much lower (cf. fig. 5.3). The maximum value of the coercive force of the material of fig. 5.1 is nevertheless high, about  $5 \times 10^3$  oersted; the appearance of the maximum at

Fig. 5.1



Temperature dependence of observed and ideal coercive forces of barium ferrite; fields in oersted. After Rathenau *et al.* (1952).

Fig. 5.2



Hysteresis curves of sintered barium ferrite. (a) Material with small crystallites, (b) with larger crystallites. Broken curves, pure rotation. After Rathenau *et al.* (1952).



about 250°C is ascribed by Went *et al.* (1952) to a balance between the number of domain walls, which decreases at higher temperatures due to an increase of the critical size, and their mobility, which increases.

Jongenburger (see Casimir 1959) has made indirect measurements of the second order crystal anisotropy constant of Ferroxdure, and found that it is at most 1% of  $K$  in the temperature range 20°K to room temperature. This result, as well as the magnitude of  $K$  itself, has been discussed by Smit (see Casimir 1959).

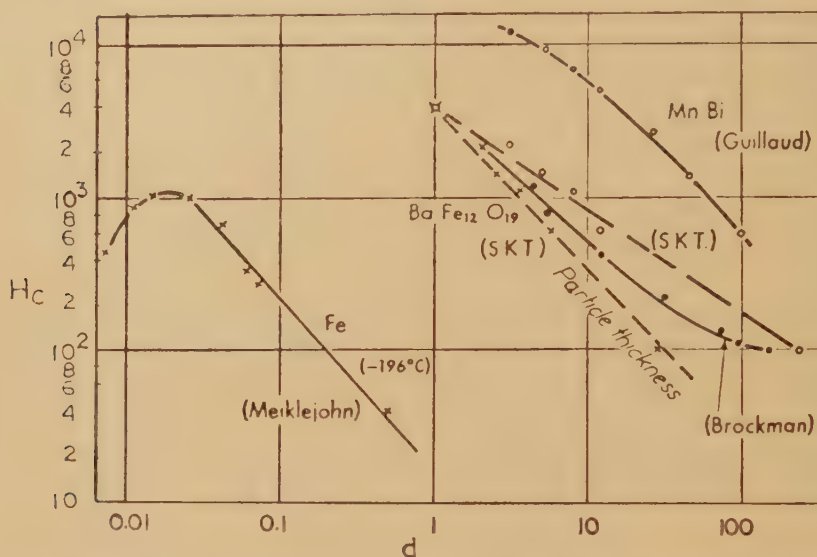
Another way in which nucleation of domain walls in the sintered material may be demonstrated is by measuring the hysteresis curve. Figure 5.2, due to Rathenau *et al.* (1952, cf. also Rathenau 1953) shows such curves, both for fine grained material (*a*), formed by sintering at low temperatures, and for coarser material (*b*). For the latter strong deviations from the curves for pure rotation (shown broken in fig. 5.2) occur in positive fields of the order  $4\pi I_0$ , where domain walls begin to nucleate. Rathenau (1953) also investigated the wall nucleation by measurements of the initial permeability. He concluded that the walls, once formed, which is easiest at low temperatures or near the Curie point where the critical size is smallest, are relatively stable. For a specimen with fine grains the permeability approaches the rotation-only value, about 1.2, at temperatures where the critical size, proportional to  $\sqrt{K/I_0}$ , is largest, but increases at low temperatures and near the Curie point, implying a decrease of magnetic hardness, as in fig. 5.1.

The earlier investigations on Ferroxdure were carried out on isotropic materials, but Rathenau *et al.* (1952) obtained an anisotropic material in which the hexagonal crystal axes had been magnetically aligned. The powders, after orientation, are compressed in the presence of a magnetic field and finally sintered by firing at a controlled high temperature. The firing process is found to improve the anisotropy since it destroys mis-oriented crystallites. The anisotropic material produced in this way was stated to have a  $(BH)_{\max}$  value  $3.0 \times 10^6$  gauss-oersted. A more complete account of the production and properties of anisotropic Ferroxdure II and III is given by Stuyts *et al.* (1954). They find that, whereas the heat treatment giving optimum remanence parallel to the direction of alignment involves sintering at a high temperature, the same process reduces the coercivity due to the particle size increase. According to the requirements a high remanence, low coercivity material (Ferroxdure II) or a low remanence, high coercivity material (Ferroxdure III) may thus be produced by controlling the firing temperature. At that time (1954) the best  $(BH)_{\max}$  value obtained was  $3.5 \times 10^6$  gauss-oersted for Ferroxdure II (see also Brockman and Steneck 1954).

Quite independently of the Dutch investigations a very similar programme led to the development of sintered barium ferrite magnets by Fahlenbrach (1953) and Fahlenbrach and Heister (1953, 1954). The magnetic properties of the isotropic and anisotropic materials Koerox are very similar to those of Ferroxdure, for example, maximum energy

products about  $3 \times 10^6$  gauss-oersted (see also Fahlenbrach 1956). Investigations aiming at high maximum energy products in oriented barium ferrite magnets have also been reported from other places. The materials Ferrimag V and Indox V, similar to Ferroxdure II, are stated by the manufacturers to have  $(BH)_{\max} = 3.5 \times 10^6$  gauss-oersted.

Fig. 5.3



Size dependence of coercive force of barium ferrite and other materials.  $H_c$ , coercive force, oersted;  $d$ , particle size,  $\mu$ . After Sixtus *et al.* (1956).

A very extensive investigation of the magnetic properties of sintered barium ferrite magnets has been reported by Sixtus *et al.* (1956). By altering the particle size by controlled milling and sintering, the coercive force of the specimens could be varied over the wide range  $5 \times 10^2$  to  $4 \times 10^3$  oersted, the last value being obtained after milling for 142 hours and sintering at 1000°C. The observed dependence of coercivity on grain size is shown in fig. 5.3, which also includes additional unpublished data of Brockman, Beck and Steneck which were unobtainable in detail, and the results on iron and MnBi powders discussed in § 3. The packing density was found to have little effect on the coercive force, as expected if magnetocrystalline and multidomain effects are important, but the degree of alignment of the anisotropic specimens has a larger effect. For specimens in the as-pressed state the ratio  $\eta$  of the coercive forces of non-oriented to that of oriented specimens had a value 1.2, implying that the magnetization changes are by wall motion or possibly incoherent rotations. After heat treatment in  $O_2$  at 1000°C the coercivities increase

and their ratio  $\eta$  decreases to a value close to 1.0, implying smaller crystallite sizes and hence a greater importance of rotational magnetization changes.

Sixtus *et al.* (1956) also measured the temperature variation of the coercive force and observed this to have a maximum near 300°C, in agreement with Went *et al.* (1952). This maximum is here ascribed to internal demagnetization effects, arising from the plate-like shape of the crystallites, as well as to the temperature variation of the critical size (Went *et al.* 1952). Measurements were also made of the reversible permeability, and for the specimens with the highest coercive force the initial permeability is about 1.2, in good agreement with a rotation-only value and with Rathenau's (1953) results. Elsewhere higher permeability values were observed.

Tenzer (1957) later investigated the temperature variation of the remanent magnetization of barium ferrite. Reversible and irreversible changes were measured; the first were proportional to the changes of the saturation magnetization. This result was taken to imply that the material is in the single-phase state. The temperature variation of the magnetic properties has also been investigated by Schwabe (1957). He finds that for anisotropic barium ferrite magnets the remanence changes are reversible over the approximately horizontal portion of the demagnetizing curve, but partly irreversible over the approximately vertical portion.

Apart from measurements of the basic magnetic properties of barium ferrites there have been two other types of experiments on these substances, namely domain and high frequency investigations. Powder patterns were observed on materials with rather large grains by Wijn (1953) and by Elschner and Andrä (1955). The last observed dagger shaped patterns, implying the presence of 180° domain walls which resemble closely those frequently observed on hexagonal cobalt. Sixtus *et al.* (1956) carried out similar measurements, both on materials with large grains (platelets of thickness above 10  $\mu$ ) and smaller ones (thickness below about 5  $\mu$ ). For the first 180° domain walls were again observed, and boundary movement was observed on application of a magnetic field. For specimens with smaller grains and coercivity above about  $2 \times 10^3$  oersted some domain boundaries were still observed, but no movement occurred on applying fields of the order of the coercive force. In this case a discontinuous movement of the colloids was, however, observed, and this is tentatively ascribed to rotational changes. Tenzer (1957) reports the formation of spike-like domains of reverse magnetization in coarse grained specimens; they were observed to grow on lowering the temperature due to an increase of the demagnetization field. These effects influence the irreversible remanence changes which Tenzer measured. Other powder pattern experiments on barium ferrites have been reported by Smit and Beljers (1955), Pearson (1957) and Paulus (1957), who used single crystal specimens. Craik and Griffiths (1959, see also Bates 1957) reported measurements on both large and small (about 5  $\mu$ ) grains using electron microscopical observation of the patterns, which allowed a magnification over 5000 $\times$  to be attained. For a small grain incipient



single domain effects were observed, as in Shur's work on MnBi (cf. § 3). Mayer (1957) observed domain patterns using electron mirror microscopy, and Kooy (1958) by using Faraday rotation in very thin (about  $1\ \mu$ ) transparent platelets.

High frequency investigations on barium ferrite have been reported by Wijn (1953) who measured the variation of the complex permeability for specimens with large grains and hence many domain boundaries. A domain wall resonance was observed at frequencies in the range 0.2 to 0.5 kMc/s. At higher frequencies the initial permeability decreases to approach the rotation-only value, but a low frequency resonance (at about 20–60 Mc/s) remains unexplained. Ferromagnetic resonance measurements have also been reported by Smit and Beljers (1955) and Weiss and Anderson (1955).

#### 5.4. *Other Hexagonal Ferrite Materials*

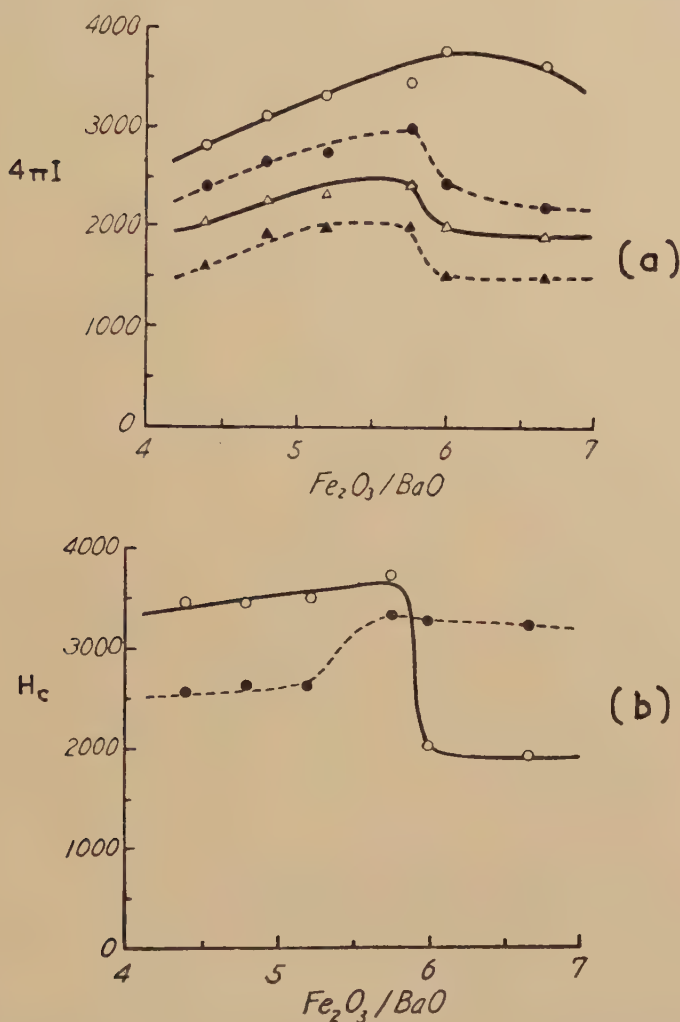
The development of pure barium ferrite with the interesting properties just described soon led to extensive research on other related materials with hexagonal crystal structure, either based on barium ferrite with additionals, or on other related ferrites with or without additionals.

Takei and Sugimoto (1955) investigated the effect of adding  $\text{As}_2\text{O}_3$  or  $\text{Bi}_2\text{O}_3$  in small quantities to barium as well as strontium ferrite ( $\text{SrO} \cdot 6\text{Fe}_2\text{O}_3$ ). It was found that the addition of 5% of the bismuth oxide has the largest effect on the maximum energy product. The additionals are believed to promote sintering, as also manifested by mechanical and microscopic observations. This work was extended in a series of papers by Okamura *et al.* (1955 a, b), H. Kojima (1955 b, c, 1956, 1957, 1958). Essentially similar results to those of Takei were obtained by using the additionals  $\text{Bi}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  and other oxides in barium, strontium and lead ferrites. The pure materials were of composition  $\text{MO} \cdot n\text{Fe}_2\text{O}_3$ , and it was found that in some cases larger remanence and coercivity occurred for  $n < 6$  than for the standard ferrite with  $n = 6$ . For example, fig. 5.4 (a) shows that the remanence of barium ferrite with 1.5%  $\text{Bi}_2\text{O}_3$  has a maximum when  $n = 5.5$ , and fig. 5.4 (b) that the coercive force of these particular specimens (prepared by sintering at  $1150^\circ\text{C}$  for 15 minutes) is also larger when  $n < 6$ . The many other results shown in this and the other figures of H. Kojima (for example, that the addition of  $\text{Bi}_2\text{O}_3$  increases the coercive force only over a part of the range of  $n$ ) shows that the effects of the additionals are not always just to promote sintering and hence grain growth. H. Kojima (1957) reports results of microscopical investigations for lead ferrite specimens; he found that the crystallites were of a hexagonal plate like shape, with a maximum diameter about 10–20  $\mu$  and thickness about 0.1  $\mu$ .

Whereas H. Kojima (1955 c) found that the effect on the coercive force of adding up to 5%  $\text{Al}_2\text{O}_3$  to barium, strontium and lead ferrites is particularly important, giving coercivities up to  $4 \times 10^3$  oersted, Guillaud and Villers (1956) obtained even higher values, up to about  $10^4$  oersted, by increasing the Al content up to as much as 15%  $\text{Al}_2\text{O}_3$ . The increase is

found to be a result of grain size *reduction*, in contradiction to Takei and Sugimoto's (1955) observations with  $\text{Bi}_2\text{O}_3$  additions. Guillaud also found that the saturation magnetization and hence the remanence are reduced as the Al content increases, due to a relative change of the sub-lattice moments.

Fig. 5.4

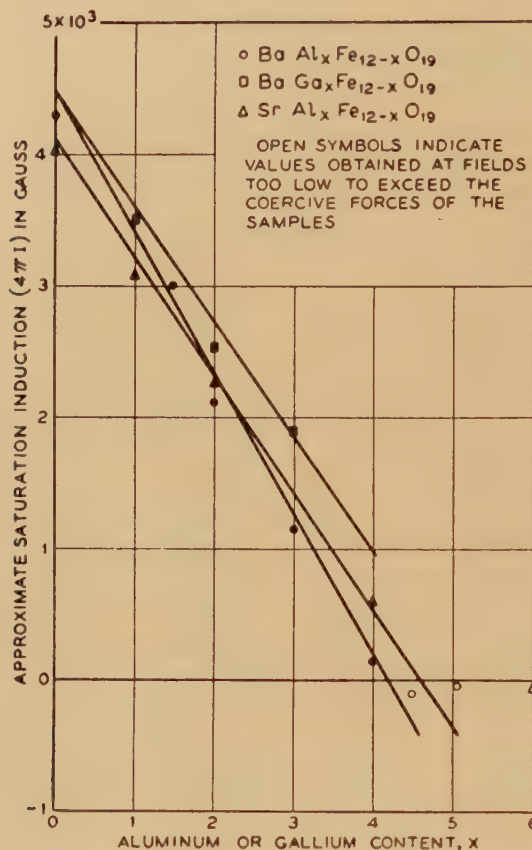


Properties of barium ferrites with additions. (a) Saturation magnetization and remanent magnetization ( $\times 4\pi$ ); circles, saturation; triangles, remanence; full lines, 1.5%  $\text{Bi}_2\text{O}_3$ ; broken lines, no additions. (b) Coercive force; full lines, 1.5%  $\text{Bi}_2\text{O}_3$ ; broken lines, no additions. After Okamura *et al.* (1955 a).

In another series of investigations Van Uitert and associates prepared a wide range of mixed barium, strontium and lead ferrites based on both  $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$  and on  $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3 \cdot 2\text{Fe}_3\text{O}_4$  which also has the hexagonal

crystal structure (Wijn 1952, Braun 1952 a, 1957). Van Uitert *et al.* (1957) prepared  $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3 \cdot 2\text{MFe}_2\text{O}_4$  with  $\text{M} = \text{Mg, Ca, Mn, Co, Ni, Cu, Zn}$ , mixtures of these and other related materials. In some cases the saturation magnetization increases above the value for the pure ferrite, e.g. 5000 cf. 4650 for the induction of the material with  $2\text{M} = \text{Fe} + \text{Zn}$ . The variation with composition was investigated by Van Uitert and

Fig. 5.5



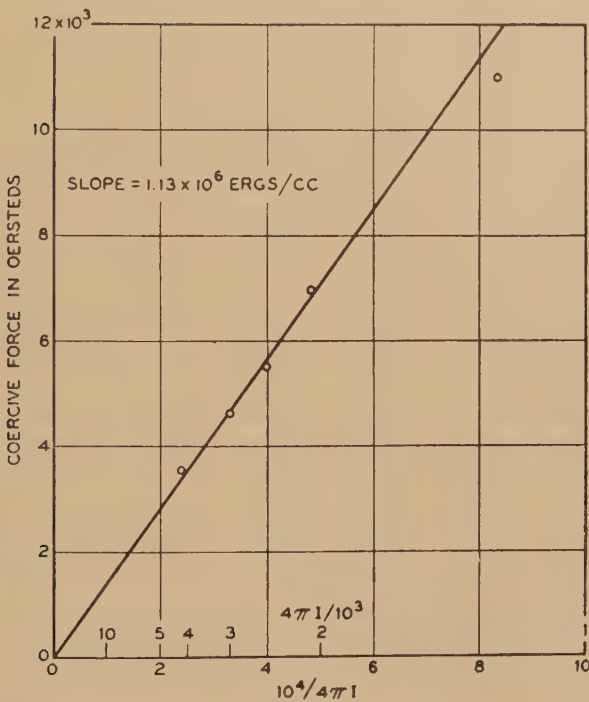
Variation of saturation with Al or Ga content. After Van Uitert (1957).

Swanekamp (1957) for many other materials whose compositions can not all be quoted here. A decrease of the saturation magnetization was observed in many cases, particularly if aluminium is substituted, in agreement with Guillaud and Villers (1956). If enough Al is added, the saturation magnetization is frequently found to pass through zero at a compensation point, and large values of the coercive force are thus expected for these compositions. Thus, fig. 5.5, due to Van Uitert (1957), shows the variation of the saturation induction for  $\text{Ba}(\text{Sr})\text{Al}_x(\text{Ga}_x)\text{Fe}_{12-x}\text{O}_{19}$ .



which is seen to be very small when  $x$  is close to 4. Coercive forces up to  $2.6 \times 10^4$  oersted were here observed even after incomplete saturation. They were measured for fine grained ( $0.8 \mu$ ) oriented specimens, and fig. 5.6 shows the variation of  $H_c$  with  $10^4/4\pi I_0$  for substituted barium ferrites. The observed linear dependence is in agreement with expectation, the coercive force being determined by magnetocrystalline anisotropy. However, the observed slope of the line of fig. 5.6 is less than predicted for rotational processes, and the variation of the anisotropy constant and the critical size with composition should also cause deviations from linearity. As elsewhere, an important contribution to the magnetization process is undoubtedly made by wall motions in these sintered materials.

Fig. 5.6



Variation of coercive force with inverse saturation magnetization in the substituted barium ferrite specimens of fig. 5.5 and others. After Van Uitert (1957).

The increase of the anisotropy field in barium ferrite substituted with aluminium causes an increase of the ferromagnetic resonance frequency in the absence of an applied field. Weiss (see Van Uitert 1957) has observed resonance above 50 kMc/s, and du Pré, de Bitetto and Brockman (1958) have extended the range of no-field resonance to 90 kMc/s by Al substitution in barium and strontium ferrites.

Experiments on lead ferrites  $\text{PbO} \cdot n\text{Fe}_2\text{O}_3$  with or without additionals have been reported by Berger and Pawlek (1957) and Pawlek and Reichel (1957). Over the optimum range of sintering temperatures (about  $1000^\circ\text{C}$ ) the remanence was found to be largest at  $n=4$ , the coercivity at  $n=6$  or 7 and the maximum energy product at  $n=4$ . These results confirm in general those of Kojima referred to above. It was further found, also in agreement with the Japanese work (Kojima 1956, fig. 5) that the addition of  $\text{SiO}_2$  has beneficial effects both on the remanence (up to about 0.7%) and the coercivity, leading to an optimum  $(\text{BH})_{\text{max}} 1.2 \times 10^6$  gauss-oersted for an isotropic mixed lead ferrite.

Another development in the field of mixed hexagonal ferrites is concerned with the work of Jonker *et al.* (1956, 1957) on mixed barium ferrites. Some of these, such as  $\text{Ba}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$  and  $\text{Ba}_2\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$ , have a negative anisotropy coefficient and hence an easy plane of magnetization, with resulting magnetic softness which makes these materials very useful as high frequency core materials; they are produced under the trade name Ferroxlana (see also Stuijts and Wijn 1958, Braun 1957). Others of these ferrites, such as  $\text{Ba}_3\text{Mg}_2\text{Fe}_{24}\text{O}_{41}$ , are magnetically hard, having a positive anisotropy coefficient which is, however, lower, as is the coercivity, than that of the unsubstituted Ferroxidure. Here is a group of materials whose coercivity and other magnetic properties can be controlled by judicious substitution.

For some of these materials, such as  $\text{Ba}_2\text{Co}_2\text{Fe}_{12}\text{O}_{22}$  (see Casimir 1959), the anisotropy is more complex than can be represented by a positive or negative first anisotropy constant, and the second order constant as well as the azimuthal anisotropy must then also be included. At some temperatures (e.g. below  $215^\circ\text{K}$  for the above material) the easy directions of magnetization then lie on the surface of a cone, an intermediate stage between Ferroxlana and Ferroxidure-like behaviour. This effect can be controlled by even more complex substitutions.

Other work on substituted hexagonal ferrites has been reported by Summergrad and Banks (1957), who substituted La and Na, K or Rb for Ba in  $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ , Mones and Banks (1958; Al, Ga, Cr, Zn, Mg, Ti substituted for Fe), Deschamps and Bertaut (1957; La, Pr, Nd, Sm, Eu substituted for Ba), Bertaut, Deschamps and Pauthenet (1958; Al, Ga, Cr for Fe; see also Bertaut, Deschamps, Pauthenet and Pickart 1959) and Gorter (see Casimir 1959; Co and Ti for Fe). The applicability of these materials can hardly yet be foreseen.

## § 6. FERROMAGNETISM AND SUPERPARAMAGNETISM OF DILUTE ALLOYS

One of the most direct ways in which the relation between magnetic hardness and magnetization processes in ferromagnetic particles may be demonstrated is by studying the properties of 2-phase alloys, containing a small amount of a ferromagnetic component. This may be either introduced

deliberately or may be present as an impurity. If, for example, the two phases are immiscible below some temperature, then, on ageing below this temperature, the ferromagnetic phase precipitates and the coercivity is found to increase to quite high values. In the first stages of this process the precipitated particles are, however, too small for ferromagnetic behaviour to be developed, and the material exhibits superparamagnetism.

### 6.1. *Early Investigations on Ferromagnetic Impurities*

An early investigation on alloys of palladium and platinum containing up to 10% cobalt was described by Constant (1929, 1930). Large coercive forces (about 400 oersted) were observed for the Pd alloys in a hard drawn state. An annealing treatment caused the coercivity to be reduced to about 100 oersted. These results are rather inconclusive since Pd and Co here form a solid solution. The effect of cold working might have been to produce fluctuations in composition as envisaged by Bitter (1931, see also Bitter and Kaufmann 1939, Bitter, Kaufmann, Starr and Pan 1941), leading to the formation of cobalt rich regions, in which magnetic hardness is developed. Annealing of the alloys would then reduce the fluctuations and hence the hardness; this might also arise as a result of the production and relief of internal stresses.

The discovery of magnetic hardness in dilute alloys led Constant (Constant and Formwalt 1939, Constant *et al.* 1943, Constant 1945) to investigate the magnetic properties of weakly magnetic materials containing minute iron impurities. The remanent magnetization values of the specimens of brass, silver, copper, bismuth, cadmium, etc. were found to range from 0.1 to  $820 \times 10^{-4}$  gauss, giving an indication of the amount of iron present. The specimens were cold worked to produce precipitation of the impurity; subsequent annealing in controlled atmospheres caused a resolution of the impurity and a loss of ferromagnetism. That the appearance of body centred iron inclusions is responsible for the ferromagnetic properties of an impure copper specimen was demonstrated by Smith (1940, see also Gordon and Cohen 1940). He observed the appearance of x-ray lines corresponding to a b.c.c. structure for the specimen after cold working or extensive ageing, but not after prolonged annealing. It was suggested that during the initial stages the iron forms f.c.c. precipitates which are coherent with the Cu matrix, and that cold working causes the precipitates to break away and to form the stable ferromagnetic b.c.c. phase. A more recent investigation on a Cu-Fe alloy (2.4% Cu) has been reported by Denney (1956), who found that prolonged ageing alone could not induce ferromagnetism in his specimens, and that this only appeared after subsequent cold working, when b.c.c. precipitate structure was also established. The fully developed iron precipitates (presumably beyond the stage of optimum magnetic hardness; see below) were found to have a plate-like shape and a size less than about  $10 \mu$ .

The measurements of Constant and Formwalt (1939) were carried out by means of Helmholtz coils, which enabled the remanence after saturation in



fields of several thousand oersted, as well as the reverse field  $H_R$  required to reduce the remanence to zero, to be determined. For the specimens investigated the values of  $H_R$  were as follows: silver, 90 oersted; copper, 200 oersted; bismuth, 300 oersted; brass, 500 oersted. By means of a second pair of Helmholtz coils, providing fields up to 1000 oersted, the complete hysteresis curves and the coercive force  $H_c$  were also determined. The ratios  $H_R/H_c$  were found to be large, for example, 4 for copper. As has been pointed out several times (e.g. by Wohlfarth 1958) large values of this ratio imply a large variation of the magnetic hardness of the individual particles, which is not surprising for specimens containing ferromagnetic precipitates at various stages of formation. Constant also came to the conclusion that some of these precipitate particles are very hard, from the observation that it was difficult to obtain saturation even in fields 1000 oersted, and that high fields were also required for the complete reversal of the remanent magnetization. These findings are confirmed by the later work discussed below.

Other measurements on ferromagnetic impurities have been reported. Schröder (1939) carried out measurements on Zn-Al alloys containing iron impurities, the remanence being about  $10^{-4}$  gauss. The remanence coercivity  $H_R$  for one sample was 570 oersted. The ratio  $j_r$  of remanence to saturation was found to be surprisingly high, almost 0.9, which would indicate, as Schröder in fact deduced, that the iron impurities form elongated, partially aligned particles. On the other hand, it may be that the estimates of the saturation magnetization were low, due to the difficulty, referred to above, of attaining complete saturation. Drigo and Pizzo (1949) reported results for the remanence, saturation and coercive forces  $H_R$  and  $H_c$  of a wide variety of impure metallic and non-metallic materials. The reported saturation values ranged from 0.005 to  $600 \times 10^{-4}$  gauss, the  $j_r$  values from 0.2 to as much as 0.9, and  $H_R$  from 200 to 1200 oersted, with a wide variability of  $H_R/H_c$ .

Great magnetic hardness has also been observed in an Ag-Fe alloy (5000 oersted coercive force according to Zumbusch 1935, who gives no further details) and a 7% Nd-Fe alloy (4300 oersted, Drozzina and Janus 1935).

## 6.2. *Later Measurements on Dilute Alloys*

The developments in fine particle theory discussed in § 2 were soon realized to be relevant to the magnetic properties of dilute alloys, and led to the recent and more systematic studies of these properties, to be described.

Hobson and Osmond (1948, cf. also Hobson *et al.*, 1948) investigated the properties of chromium-nickel austenitic stainless steel specimens which had been rendered ferromagnetic by cold drawing into wires, causing the precipitation of the body centred ferritic phase (these wires are sometimes used for magnetic recording purposes). The ferromagnetic precipitates, partially oriented along the wire direction, were shown from the electro-acoustical properties of the wires (ratio of maximum to minimum recordable undistorted signal strengths, maximum recordable frequency) to be

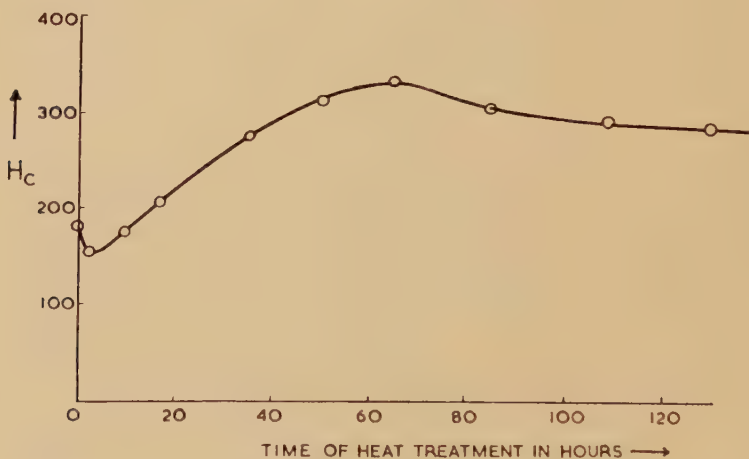
fairly evenly distributed in the austenitic matrix, to have a width between about  $0.03$  to  $0.1 \mu$  and a length less than about  $3 \mu$ . With such elongations (axial ratios  $m$  above about 10) the widths may well be below the critical values for single domain behaviour ( $0.09 \mu$ , approximately, for Fe particles with  $m=10$ ; cf. § 2), and the observed coercive forces up to about 500 oersted are then easy to understand. They are doubtless kept to such relatively low values as a result of shape anisotropy and other fluctuations, as well as by effects of incoherent reversals (cf. § 2).

This work on stainless steel wires has been continued by Sucksmith (1952). He measured the coercive force and reduced remanence  $j_r$  for wires in the as-drawn state, after heat treatment at between  $450^\circ$  to  $550^\circ\text{C}$ , and after cold-rolling which may be followed by further heat treatment. The coercivity was found to increase during the treatment at  $500^\circ\text{C}$ , reaching a value 500 oersted after 5 hours, but then to drop to lower values as the treatment proceeded, reaching 220 oersted after 50 hours. The cold rolling also reduced the coercivity. The value of  $j_r$ , initially as much as 0.96, pointing to almost perfect alignment, also decreased after the heat treatment had proceeded for some time, and the cold rolling again reduced  $j_r$ . Heating at  $550^\circ\text{C}$  also reduced  $j_r$  to low values. The heating results may be interpreted in terms of the formation of ferritic precipitates of optimum size, causing the initial coercivity increase, and their continued re-resolution by further heating, causing the subsequent drop of the coercivity as well as of  $j_r$ . The precipitation and growth of ferrite particles by cold working also decreases the coercivity and  $j_r$ , although the saturation magnetization increases as more ferrite is formed. The mechanical working also changes the particle shape, and a quantitative discussion of the results is not easy. Nevertheless, these experiments contain the principal ideas of most of the subsequent investigations on dilute alloys. The main disadvantage of experimenting with these specimens is that the ferromagnetic component is present in relatively large amounts, so that particle interactions are serious. More dilute alloys are more advantageous from this point of view.

Bate *et al.* (1953, 1955) thus investigated Cu-Co and Cu-Fe alloys containing up to 2% of the ferromagnetic component. The specimens were heat treated at various temperatures for different lengths of time, and the magnetization measurements were carried out using a torsion apparatus. The process of precipitation of the ferromagnetic phase can be followed from the observed variation of the coercive force  $H_c$  with ageing time. This is shown in fig. 6.1 for a 1% Cu-Fe alloy treated at  $650^\circ\text{C}$ . The initial variation of  $H_c$  is anomalous; it could arise as a result of strain relief. The attainment of a maximum coercivity about 340 oersted, followed by a decrease to lower values after prolonged ageing, is due to the growth of the precipitate particles, which thus pass from partial superparamagnetic to optimum single domain and finally, possibly via a 'curling' type of structure, cf. § 2, to multidomain behaviour. At any time particles in all stages are likely to be present, and it is only their relative numbers which change

during the process and lead to the observed behaviour. Bate *et al.* also measured the variation of the remanent magnetization with the strength of a reverse magnetic field and found, as in the experiments described above, that the remanence coercivity  $H_R$  is high, reaching 1600 oersted, and that  $H_R$  may exceed  $H_c$  by large factors. Like  $H_c$ ,  $H_R$  decreases on over-ageing. These results, and the observation that saturation of the magnetization and complete reversal of the remanence require fields of many thousand oersted, show quite clearly that a very hard magnetic constituent, which may reasonably be identified as containing single domain particles, is present in the non-magnetic matrix over a long period of the ageing process. The fact that high fields are required for saturation may, however, also point to the presence of a large fraction of very small superparamagnetic particles which, as seen below, relation (6.3), are very difficult to saturate.

Fig. 6.1

Coercivity of copper-iron alloy. After Bate *et al.* (1955).

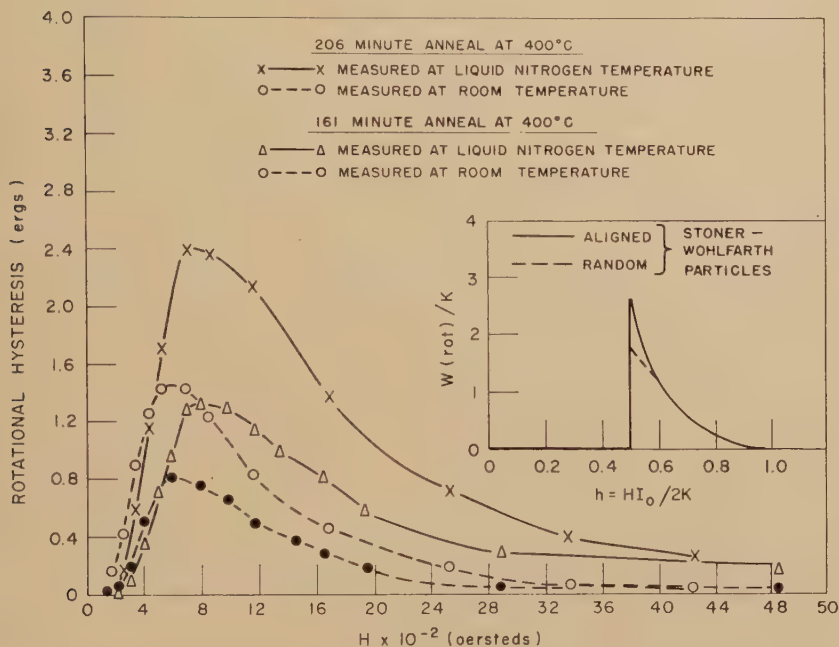
To test this view it is necessary to investigate the law of approach more fully, as discussed later. The fact that the remanence is difficult to reverse seems, however, to provide stronger evidence for the presence of hard single domains.

An extensive investigation of the initial stages of precipitation in a Au-Ni alloy containing 24% Ni has been described by Berkowitz and Flanders (1957). After initial annealing at 900°C the specimens were quenched and then aged for up to 3½ hours at 400°C. The measurements described include those of torque curves, the saturation and remanent magnetizations and the rotational hysteresis. The torque curves show that a magnetic anisotropy is developed in fields above about 500 oersted and after ageing for at least 2 hours. The saturation measurements were used to estimate the ratio of the amount of nickel precipitated to the equilibrium amount corresponding to the phase diagram, and values less than 1% were



obtained after  $3\frac{1}{2}$  hours ageing. The remanence measurements were used to estimate the fraction of the precipitate particles in the single domain state, and a value 46% was obtained after the above ageing time, but 62% after only 3 hours. The rotational hysteresis was measured at room and liquid nitrogen temperatures as function of field strength, and the measured curves are shown in Fig. 6.2; the inset gives theoretical curves for single domain particles with constant uniaxial anisotropy. The differences between the theoretical and observed curves, as well as between the respective rotational hysteresis integrals  $R$ , defined by relation (2.11), involving factors between 2 and 3, provide some evidence as to the magnetic state of the precipitates.

Fig. 6.2

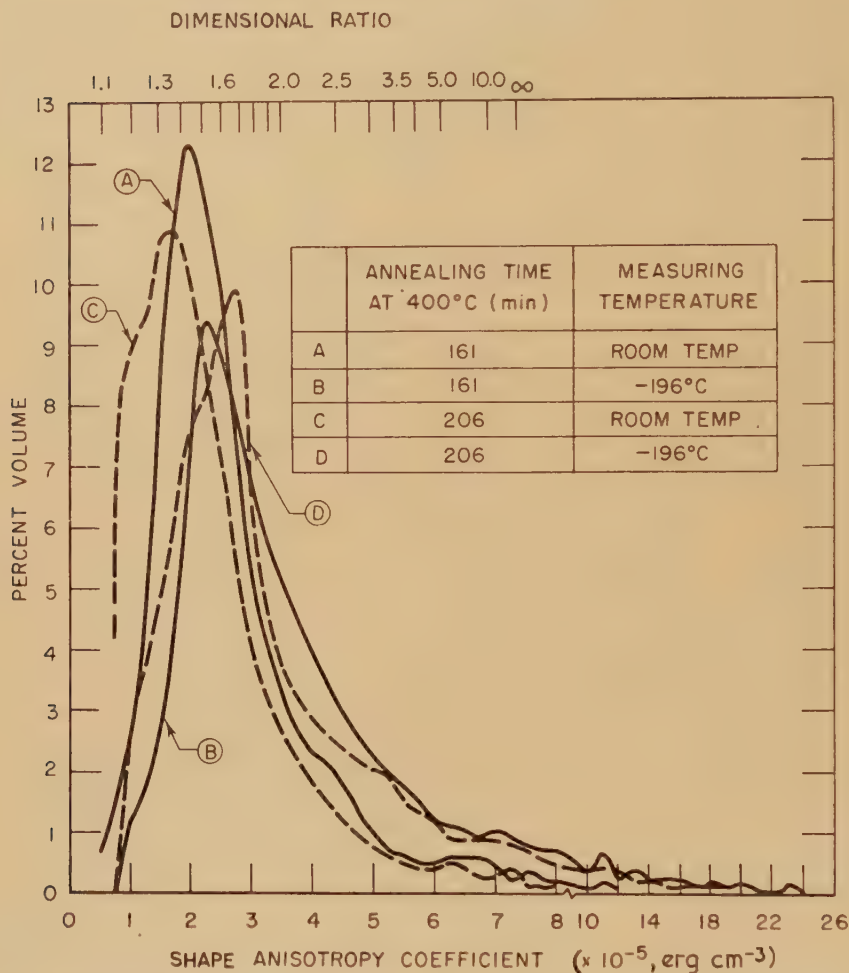


Rotational hysteresis of Au-Ni. After Berkowitz and Flanders (1957).

These results were analyzed as follows: The low field torque curves show that here there is a random distribution of the easy axes of magnetization; but the anisotropy developed in higher fields is ascribed to a small degree, about 6%, of orientation of the easy axes in the [100] direction of the (110) planes. The rotational hysteresis curves, cf. fig. 6.2, showing that individual coercive forces up to 3 to  $4 \times 10^3$  oersted are active, as well as the bulk coercive force measurements of Köster and Dannöhl (1936) and Gerlach (1949), are taken as evidence that shape anisotropy is important in governing the magnetic properties of the precipitates; at liquid nitrogen temperatures the crystal anisotropy of nickel is, however, large, and may

also influence the observed behaviour. The deviations between the observed and calculated rotational hysteresis curves imply that there is a wide variation of the individual coercive forces of the precipitate particles, due, it is thought, to particle shape variations. By analyzing these

Fig. 6.3



Shape anisotropy distribution in Au-Ni. After Berkowitz and Flanders (1957).

deviations it was possible to derive distribution curves for the volume fraction of particles whose shape anisotropy coefficient (or dimensional ratio) lies between given limits. The results are shown in fig. 6.3; this indicates that a considerable fraction of the particles has almost spherical shape, but that the fraction of quite acicular particles, with dimensional ratios between 2 and 3, say, is by no means negligible. The analysis also shows that during

the ageing process the non-acicular particles grow faster than the more acicular ones. The differences between the observed and calculated rotational hysteresis integrals suggest (cf. § 2) that some of the precipitates may be too large to be single domains or for the magnetization reversals to be coherent. The integrals are larger after prolonged annealing when the fraction of non-acicular particles is also higher; the remanence data show that these are more likely to be multidomains. The particle sizes were very roughly estimated, and were all found to lie in the range  $0.1$  to  $0.2\mu$ . Berkowitz and Flanders (1958) also carried out electron microscope observations on their Au-Ni specimens, and found that the precipitation is confined to a thin layer (about  $5\mu$  thick) of the surface, that the particle sizes extended down to  $0.04\mu$  and that little shape anisotropy or orientation was detectable by this means, although there was the magnetic evidence for these effects.

Berkowitz and Flanders (1958, 1959) also investigated the precipitation of iron in  $\beta$ -brass. The iron rich particles were found from torque measurements to be single crystals with b.c.c. structure and with the same crystal habit as the matrix, but with slight elongations along the  $[111]$  directions. The coercive forces and rotational hysteresis integrals depended on the direction of measurement, whether in the (100) or (110) planes; after prolonged annealing the measured values were 50 and 150 oersted respectively for the coercive force and  $1.13$  and  $0.70$  for  $R$ . The low coercive forces may be evidence for the particles being large multidomains, but, by following the ageing treatment from its earliest stages, superparamagnetism was detected in particles as small as  $0.0015\mu$  which were then observed to grow through single domain and multidomain sizes.

The magnetic properties of dilute alloys of the type under discussion have been seen to be strongly influenced by the shapes of the precipitate particles. These may be determined by the magnetic methods described above or by direct electron microscope observations, which seem, however, to be difficult and often inconclusive. Bean *et al.* (1957) have used ferromagnetic resonance methods to determine the shapes of the precipitate cobalt rich particles in a 2% Cu-Co alloy. The shapes determine the demagnetization factors of the particles, and hence influence the condition for ferromagnetic resonance absorption. This was measured at different stages of ageing, for which the particle sizes could be estimated using the magnetic methods discussed below. It was found that the ferromagnetic precipitates come down initially (size about  $0.0025\mu$ ) almost spherical in shape, but that growth of the particles is accompanied by a tendency towards plate-like formation; for particles of estimated size about  $0.03\mu$  the estimated dimensional ratio of the equivalent oblate spheroid is about 1.1. Rodbell (1958), after confirming that the cobalt rich particles have a f.c.c. structure (see papers by Becker 1957, and others, discussed below), showed that their longest axes define planes parallel to the (100) planes of the copper matrix with which the precipitates are in this state coherent. Rodbell also used resonance methods to measure the crystal anisotropy constants of the



cobalt rich (10% Cu) precipitates, and found that  $K_1 = -8.6 \times 10^5 \text{ erg cm}^{-3}$ ,  $K_2 \simeq K_1/5$  at room temperature. This  $K_1$  value is much smaller than the extrapolated value for pure bulk f.c.c. cobalt; the deviation may be due in part to the presence in the precipitates of 10% Cu. Bean, Livingston and Rodbell (1959 a, b) measured the anisotropy constants of cobalt in copper, using both resonance and torque methods, and covering a range of temperatures and particle sizes. At 4°K,  $K_1 = -1.17 \times 10^6 \text{ erg cm}^{-3}$  for particles of size between 0.0021 and 0.0077  $\mu$ . At higher temperatures  $K_1$  varies slightly with size, due, it is believed, to a slight variation of the saturation magnetization. At these temperatures, also, the torque and resonance values of  $K_1$  differ slightly.

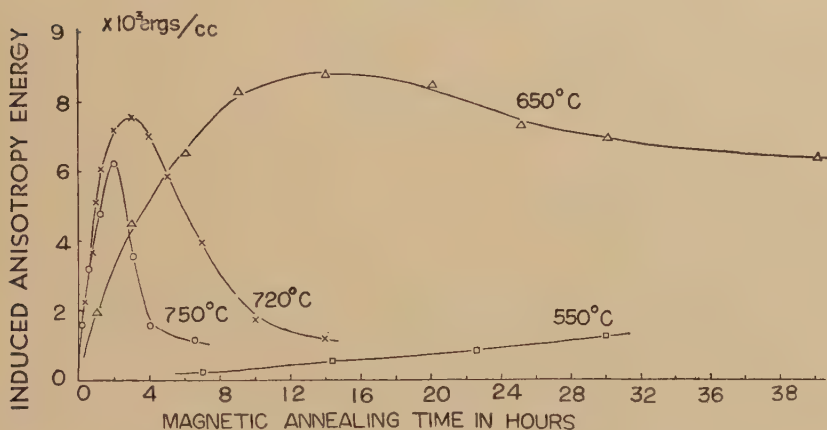
### 6.3. *Magnetic Annealing*

The influence of a magnetic field applied during the precipitation process in dilute alloys has been investigated very extensively by Mitui. He (Mitui 1958 a, see also Mitui and Miyahara 1955) investigated a 2% Cu-Co alloy treated at between 550° to 750°C in fields up to  $8 \times 10^3$  oersted for times up to about 40 hours. The induced uniaxial anisotropy constant  $K_U$  was measured by means of a torque magnetometer. For a specimen aged 20 hours without a field and then 4 hours with a field, both at 750°C,  $K_U$  was only  $4 \times 10^2 \text{ erg cm}^{-3}$ ; on the other hand, immediate ageing in the field raised  $K_U$  to  $4 \times 10^3 \text{ erg cm}^{-3}$ . This result shows that the orienting effect of the field is most effective in the early stages of ageing. The variation of  $K_U$  with annealing time, shown in fig. 6.4, indicates also that the magnetic annealing process is most marked when ageing has reached a critical stage. As the coercive force, which varies somewhat as in fig. 6.1, and the mechanical hardness (see below) also reach maximum values at an early stage of ageing close to the maximum of  $K_U$ , it seems clear that the field applied during the heat treatment acts to orient the precipitate particles of optimum single domain size, and which, as Mitui estimates, have the right degree of shape anisotropy and dispersion. On over-ageing both  $K_U$  and the coercive force decrease as multidomains are formed, these being less alignable by the magnetic field. The change of  $K_U$  shown in fig. 6.4 can be described as an activation process with activation energy  $36 \text{ kcal mol}^{-1}$ , less than that for diffusion of Co in Cu. The induced anisotropy was also measured as a function of ageing time, reaching a maximum after 2 to 3 hours at 750°C, independently of field. These maximum values of  $K_U$  increase with the field strength, a saturation value about  $10^4 \text{ erg cm}^{-3}$  being reached in fields about  $10^4$  oersted. Mitui was also able to induce a 4-fold magnetic anisotropy in these alloys by annealing consecutively in two field directions at right angles. This treatment is, however, ineffective if it is carried out in the over-aged state. These results are not yet fully understood.

Mitui (1955, 1958 b) also carried out a series of other measurements on 2% Cu-Co. He found that the crystal structure of the cobalt precipitates is f.c.c. with lattice constant 3.61 A.U., cf. 3.55 A.U. for the copper matrix. From measurements of electrical resistance and mechanical hardness he

concluded again that the magnetic annealing treatment is most effective during an early stage of ageing, which was detected by these measurements. In this stage the mechanical hardness was also found to show some anisotropy, about 3% after treatment for 5 hours at 750°C in a field  $7 \times 10^3$  oersted. The specimens were also investigated microscopically. Optical microscopy gave inconclusive results as the over-aged particles visible do not respond to the annealing treatment. The precipitates were here found to be plate shaped with major axis about  $2 \mu$ , minor axis about  $7 \mu$  and thickness about  $2 \mu$ , and to be parallel to (111) planes of the matrix. Electron microscopy was used to detect particles of optimum size; this was estimated to be about  $0.01 \mu$  diameter and  $0.001 \mu$  thickness for the plate-like particles, which could also be seen to be partially aligned by the magnetic field. These results may be compared with those discussed elsewhere. The precise relationship between the plate-like shape of the precipitates, as detected by electron-microscopy or resonance methods, on the one hand, and the apparent uniaxial anisotropy, detected magnetically, on the other, is by no means yet clear.

Fig. 6.4

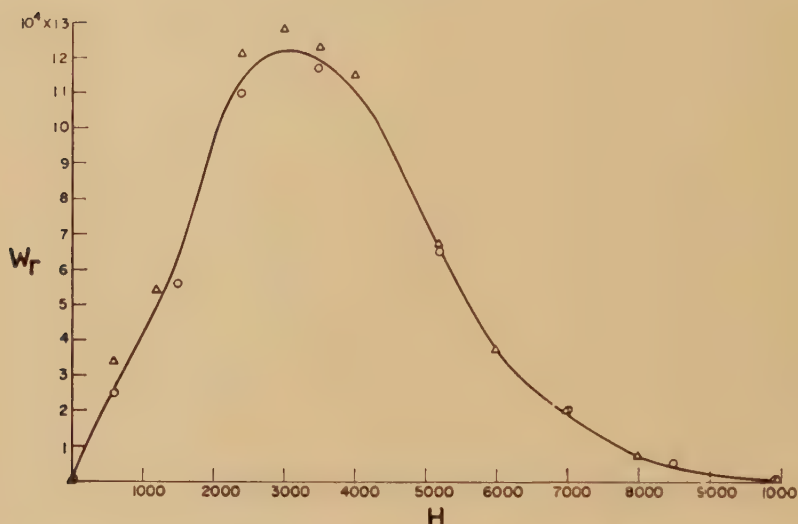


Magnetic annealing treatment of 2% Cu-Co alloy.  
Annealing field,  $3 \times 10^3$  oersted. After Mitui (1958 a).

Mitui (1956) also reported preliminary results of magnetic and mechanical hardness measurements on magnetically annealed 2% Cu-Fe alloy specimens. The hardness increased in the early stages of ageing where precipitation thus takes place. Owing presumably to the f.c.c. crystal structure of the precipitates in this stage, no ferromagnetism and, in particular, no induced anisotropy could here be detected, and  $K_U$  only appeared after about 6 hours' ageing at 700°C in a field  $5 \times 10^3$  oersted, when larger b.c.c. precipitates presumably form. The values of  $K_U$  range to about  $1.5 \times 10^3 \text{ erg cm}^{-3}$  after 30 hours.

Magnetic annealing in 2% Cu-Co has also been investigated by Becker (1958). The magnetic treatment was carried out at higher temperatures (up to 800°C), for shorter times (up to 2 hours), and in lower fields ( $10^3$  oersted) than in Mitui's (1958a) experiments. As there, the saturation magnetization reached a constant value very early in the ageing process, and thereafter the processes were thus concerned with the growth, re-solution and alignment of a constant amount of the precipitated cobalt rich phase. The maximum uniaxial torque induced by the field reached about  $10^5 \text{ erg cm}^{-3}$ , and, as with Mitui, over-ageing at the highest temperatures reduces this torque. The rotational hysteresis was also determined, and fig. 6.5 gives the results after ageing for  $\frac{1}{2}$  hour at 650°C either with a field

Fig. 6.5



Rotational hysteresis in Cu-Co.  $W_r$ , rotational hysteresis  $\text{erg cm}^{-3}$  precipitate;  $H$ , measuring field, oersted. Circles, no ageing field; triangles, ageing field  $10^3$  oersted. After Becker (1958).

or without. The two sets of data coincide, showing that the magnetic field does not produce the particle anisotropies but only causes alignment. Further, it is seen that a considerable fraction of the particles has individual coercive forces of many thousand oersted (cf. fig. 6.2). The remanent magnetization and coercive force were also measured; they pass through maxima at a critical ageing time, which differs from that corresponding to the maximum torque. Further, both remanence and coercivity are larger in the annealing direction than perpendicular to it. On the other hand, the remanence coercivity  $H_R$  is greater in the perpendicular direction, which may be understood from models of partially aligned particles (Jacobs and



Luborsky 1957, Becker 1958, Wohlfarth 1959). The general interpretation of Becker's and Mitui's data is roughly the same, in terms of growth and alignment of precipitate particles. They are assumed to be slightly elongated, the dimensional ratio 1.2 being calculated as a balance between surface tension and magnetostatic effects (Néel 1947 c). This interpretation seems, however, to be at variance with the results of those experiments, discussed above, which lead to a plate-like shape of the precipitates. It may be, as in Alnico V (cf. § 7), that these platelets are made up of a number of parallel rod shaped particles.

#### 6.4. Effects of Cold Working

The effect of cold working on the properties of stainless steel wires was discussed above. This work has been extended to other materials. Weil *et al.* (1957) measured the remanent magnetization and coercivity of drawn 1% Cu-Co wires containing cobalt rich precipitates of size about  $0.006 \mu$ . To suppress superparamagnetic effects the measured values had to be extrapolated to 0°K, and it was found that, for the reduced remanence parallel and perpendicular to the drawing direction,  $j_r^{\parallel} = 0.7$  and  $j_r^{\perp} = 0.22$ . For the coercive force  $H_c^{\parallel} = 1200$  oersted,  $H_c^{\perp} = 700$  oersted. The cobalt precipitates were shown, on the basis of the temperature variation of the coercive force (cf. Weil *et al.* 1948), to have a cubic crystal structure, in a state of epitaxy with the copper matrix. It is this state rather than the effect of shape anisotropy which is believed to lead to the observed magnetic anisotropy in this alloy.

Weil and Conte (1957, see also Weil 1959) continued this investigation on Cu-Co wires successively drawn to smaller diameters and then heat treated. For a drawn 1 mm diameter wire the reduced remanence values in the two directions are similar to those quoted above, but for the same wire drawn to 0.3 mm, containing smaller cobalt rich particles of size about  $0.004 \mu$ , no remanence was observable even at the lowest temperatures covered. Heat treating the 1 mm wire at 300°C increases the amount of precipitated cobalt and the precipitate sizes, reduces the anisotropy of the remanence and coercivity and reduces the values of both these quantities. Further treatment at 600°C continues this process, the coercivities being now only about 250 oersted, compared to 1500 oersted for  $H_c^{\parallel}$  in the as-drawn state. The grain growth induced by the heat treatment is responsible for the decrease of magnetic hardness and anisotropy. For the 0.3 mm wire heated at 300°C a curious result was observed, both the coercivity and reduced remanence having larger values perpendicular to the original drawing direction than parallel to it. This result was explained by Weil in terms of the epitaxy of the cobalt rich precipitates: the drawing aligns the [100] directions of the copper parallel to the wire, and the [100] directions of the precipitates may thus be aligned likewise. As these are difficult directions of magnetization, the crystal anisotropy would reduce the coercivity in the wire direction in relation to that perpendicular to it. The effects of

shape anisotropy, induced by the original drawing, are thus reduced in favour of crystal anisotropy effects by the subsequent heat treatment.

Measurements on drawn and heat treated wires of a 2.6% Au-Co alloy have also been reported by Weil (1958) who deduced from his results, which seem to have been inconclusive from the point of view of superparamagnetism, the variation of the amount of precipitated cobalt with treatment temperature.

Livingston and Becker (1958) also reported magnetic measurements on deformed 2% Cu-Co specimens. For a wire drawn to an elongation 12% the coercivity at 77°K rises from small values much earlier (after about 100 minutes) during ageing at 600°C than for the same wire undeformed (after about 1000 minutes). The deformation was believed to increase the magnetic anisotropy of the particles and thus to suppress superparamagnetism at an earlier stage (cf. fig. 2.3). It was concluded from initial susceptibility measurements that this induced anisotropy is uniaxial and aligned along the wire, and torque measurements confirm this view, leading to induced anisotropy constants up to  $7 \times 10^6$  erg cm<sup>-3</sup> precipitate. The induced anisotropy was shown to be almost certainly due to changes, by the deformation, of the particle shape, initially nearly spherical. Values calculated on the basis of ideally homogeneous deformations agree well, for relatively small changes, with those observed.

Lothian *et al.* (1958; see also Sucksmith 1959) have reported measurements of the coercivity  $H_c$ , reduced remanence  $j_r$  and remanence coercivity  $H_R$  in the two principal directions of cold drawn specimens of the following alloys:  $\frac{1}{2}$ , 1 and 2% Cu-Fe; 1,  $1\frac{1}{2}$ , 4% Cu-Co; 6, 9% Au-Ni. For the Cu-Fe alloys,  $H_c^{\parallel}$  increased to large values as a result of the deformation and  $H_R^{\parallel}/H_c^{\parallel}$  decreased to values close to 1;  $H_c^{\perp}$  changed little from the values for the undrawn specimens, and  $H_c^{\parallel} \gg H_c^{\perp}$  but  $H_R^{\perp}$  changed similarly to  $H_R^{\parallel}$ . The reduced remanence  $j_r^{\parallel}$  increased to large values up to 0.92 and  $j_r^{\perp}$  then decreased, pointing towards orientation of the particles once they had been transformed into the b.c.c. form. For the Cu-Co alloys both  $H_R^{\parallel}/H_c^{\parallel}$  and  $H_R^{\perp}/H_c^{\perp}$  were remarkably high, reaching almost 50 as a result of the smallness of the  $H_c$ . As the  $j_r$  values were also small, there is strong evidence for a wide spread of individual coercivities and superparamagnetism. Only for the 4% alloy drawn 96% were larger coercivities observed ( $H_c^{\parallel} = 310$  oersted), and even here  $j_r^{\parallel}$  equalled only 0.3. For the Au-Ni alloys on the other hand,  $H_R/H_c$  values were uniformly close to 1 to 1.5, and the  $j_r$  values also varied relatively little during the deformation, implying more or less random precipitate orientations. An interesting result for this system was that  $H_c^{\perp}/H_c^{\parallel}$  was always above 1, reaching about 1.5. This result might imply some cross-orientation or the effect of epitaxy plus crystal anisotropy of Weil and Conte (1957). Here and elsewhere it was more frequently observed that  $H_R^{\perp}/H_R^{\parallel} > 1$ , a result which seems reasonable (Wohlfarth 1959).

The full detailed results of these experiments are difficult to interpret, and they must eventually be considered in relation to the other data discussed earlier.

## 6.5. Superparamagnetism of Dilute Alloys

As discussed briefly in § 2, if the size of a ferromagnetic particle decreases below a critical value, depending on the temperature, the particle anisotropy and the magnitude of any applied field, the particle behaves paramagnetically as a result of the thermal fluctuations of the magnetization vectors. Néel's (1949 b) original application of this idea was to rock magnetism, and Weil (for example, 1955) and others (cf. § 3) have observed the phenomenon in powder materials, but it has also been observed in dilute alloys (for a full review, see Bean and Livingston 1959).

An early investigation of the effect in the Hg-Fe system, on samples containing about 1-2% Fe in dispersed form, was reported by Mayer and Vogt (1952). They found that when freshly prepared these samples had a very low coercive force, increasing to over  $10^3$  oersted after ageing for several hours. As ageing proceeds and the magnetic hardness increases, it was found that the saturation magnetization at room temperature also rose, from about 55% of the value for massive iron in the initial soft state to almost this value when the coercivity was 500 oersted. The Curie temperature in the initial state was also found to be low. These results were interpreted as a gradual transformation to full ferromagnetism from (super)paramagnetic behaviour. The size of the iron particles in the soft state prior to ageing was estimated from the observed approach to saturation, a method recently made more systematic as discussed below, and a value about  $0.003 \mu$  was obtained for one sample. Ferromagnetism has also been observed in Hg-Ni (Henning 1958) after heating.

Bean and Jacobs (1956) later extended the investigations on fresh iron amalgams by covering a temperature range  $4^\circ$  to  $200^\circ\text{K}$  and fields up to  $10^4$  oersted. The analysis of their data is based on the Langevin formula for the variation of the magnetization  $I$  of a paramagnetic substance with temperature  $T$  and field  $H$ ,

$$I/I_0 = L(vHI_0/kT). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6.1)$$

Here  $v$  is the mean volume of the particles, and the term 'superparamagnetism' was introduced (Bean 1955) to indicate graphically that for particles containing many atoms the magnetization in a given field is much larger than for single atoms to which (6.1) is usually applied. Earlier discussions of this phenomenon were given by Stoner (1936), Elmore (1938) and Heukelom *et al.* (1954).

At low and high  $H/T$  relation (6.1) reduces respectively to

$$I = vHI_0^2/3kT, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6.2)$$

and

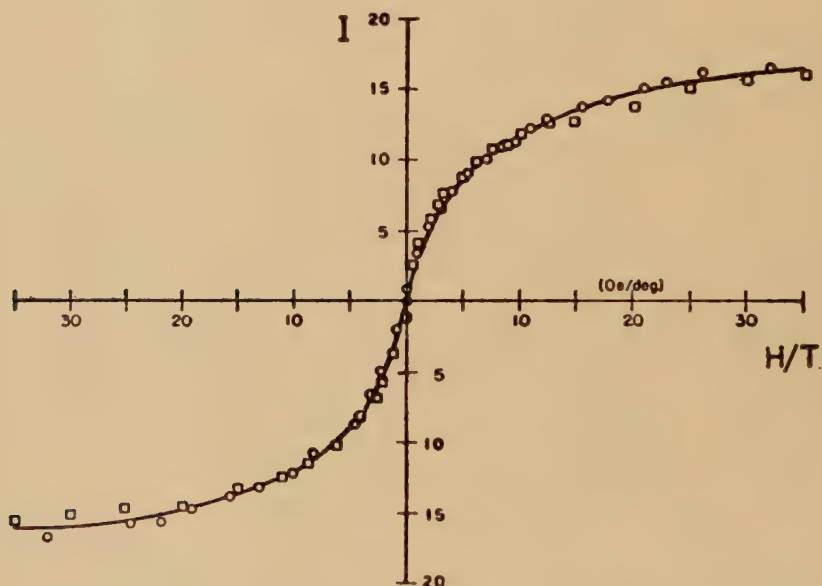
$$I = I_0(1 - kT/vHI_0), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6.3)$$

and Bean and Jacobs used these formulae for the initial susceptibility and the approach to saturation as well as the full relation (6.1) in discussing their results. Measurements at  $77^\circ$  and  $200^\circ\text{K}$  and in relatively low fields show that here the coercivity and remanence are very low, indicating that almost all the iron particles are superparamagnetic. The magnetization curves for both temperatures coincide if the magnetization  $I$  is plotted



as a function of  $H/T$ , shown in fig. 6.6, in complete agreement with the Langevin law, and thus verifying the correctness of the physical concept underlying its application to superparamagnetism. Measurements at  $4^\circ\text{K}$  on the same fresh amalgam reveal a coercive force 280 oersted and appreciable remanence, so that a considerable stabilization of the larger iron particles seems to have occurred between  $77^\circ$  and  $4^\circ\text{K}$ . From fig. 6.6 and relation (6.2) the mean particle diameter was estimated as  $0.0045\mu$ , close to Vogt's value. Bean and Jacobs' high field results at  $77^\circ\text{K}$  show that a curve relating  $I$  with  $1/H$  is linear, in agreement with relation (6.3), but at  $200^\circ\text{K}$  the curve deviates from linearity and here the full relation (6.1) must be used. Both curves seem to extrapolate to the same saturation value; the mean particle diameter estimated from the high field data was  $0.003\mu$ .

Fig. 6.6



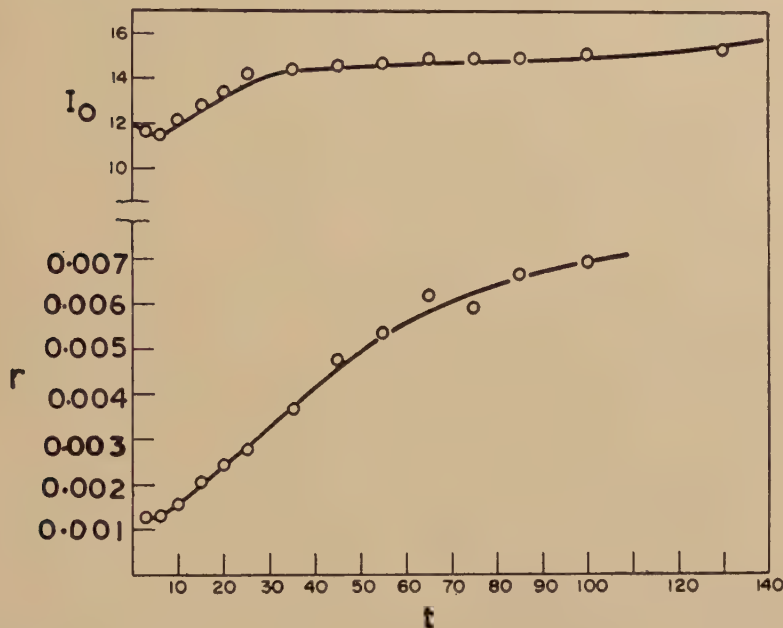
Magnetization curve of fresh iron amalgam.  $I$ , magnetization (arbitrary units);  $H/T$ , ratio field in oersted to temperature. Circles, measurements at  $77^\circ\text{K}$ ; squares  $200^\circ\text{K}$ . After Bean and Jacobs (1956).

A more recent investigation on iron and cobalt amalgams by Henning and Vogt (1957) gives results differing from those of Bean and Jacobs (1956) in that the magnetizations observed in the highest fields ( $10^4$  oersted) do not seem to extrapolate to the same saturation value at different temperatures. It may be that the observed  $I$ ,  $1/H$  curves would bend up sufficiently to reach the same saturation value at all temperatures, as Bean and Jacob's work indicates, but this is not established in Vogt's work. Henning and Vogt (1959) ascribe the decrease of  $I_0$  to a size effect similar to that occurring in the spin wave treatment of thin films

(q.v.). If the saturation magnetization is, indeed, not constant, this method of particle size analysis loses much of its value.

This problem has been considered further by Kneller (1958) on the basis of measurements on partially ordered Ni-Mn alloys (see below). He finds that the Curie temperature  $\theta$  of the ordered ferromagnetic  $\text{Ni}_3\text{Mn}$  particles present in this material after heat treatment depends on the particle size, if this is below about  $0.01\mu$ , and that it decreases with this size. At the same time, the reduced spontaneous magnetization has the same dependence on the reduced temperature  $T/\theta$  as in the bulk material. From this result Bean and Jacobs' (1956) constancy of the saturation magnetization is easily explained. The dependence of the magnetization on inverse field was, however, found to be similar in effect to that observed by Henning and Vogt (1957, 1959). For a full discussion, see Bean and Livingston (1959).

Fig. 6.7



Saturation magnetization and particle radius of Cu-Co.  $I_0$ , saturation magnetization, gauss;  $r$ , particle radius,  $\mu$ ;  $t$ , ageing time at  $650^\circ\text{C}$ . minutes. After Becker (1957).

The occurrence of superparamagnetic behaviour in a 2% Cu-Co alloy has been established by Becker (1957). By ageing at  $650^\circ\text{C}$  he found it possible to ensure this behaviour at room temperature, manifested by essentially zero coercive force and remanence, for the first 100 minutes of treatment. Low field measurements at  $77^\circ$  and  $300^\circ\text{K}$  show the same superposition of the  $I, H/T$  plots as in fig. 6.6, and the mean particle radius was thus estimated as function of ageing time. The results are shown in





Weil (1957) for similar specimens aged at 300°C. The results for the last investigation are shown in table 6.1. Here  $d(T)$  and  $f(T)$  have just been defined;  $d_\infty$  and  $d_0$  were obtained from relations (6.3) and (6.2) respectively. The table shows that  $d_0 > d_\infty$ , since at low fields the larger particles have a more pronounced effect on the magnetization, tending to conceal that of the smaller ones, the opposite being true at high fields (cf. relations (6.2) and (6.3)). By using results obtained by these methods Weil was able to draw histograms for the distribution function  $\phi(d) = \Delta f / \Delta d$ , giving the fraction of particles which are ferromagnetic with a size in a given range. As an example, fig. 6.8 gives  $\phi(d)$  for 1% Cu-Co aged at 600°C.

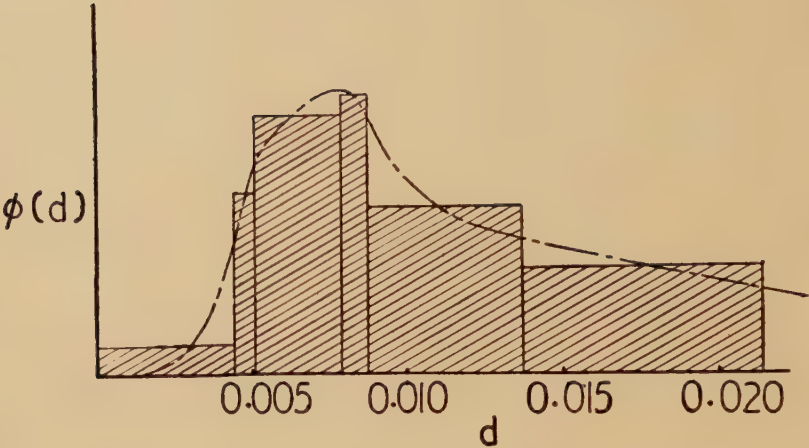
Table 6.1. Superparamagnetism in 1% Cu-Co.  $T$ , temperature;  $d$ , critical diameter for limiting superparamagnetism;  $f$ , fraction of ferromagnetic particles;  $d_\infty$ , mean diameter deduced from law of approach at high fields;  $d_0$ , mean diameter deduced from initial susceptibility. After Weil (1957).

$T^\circ\text{K}$	$d(\mu)$	$f$	$d_\infty(\mu)$	$d_0(\mu)$
2.6	0.0044	0.624	0.0046	0.0050
4.2	0.0051	0.530	0.0050	0.0060
20.4	0.0087	0.152	0.0063	0.0106
77	0.0135	0.018	0.0085	0.0168
293	0.0211	0.006	0.0125	0.0238

Similar results have also been obtained by Henning and Vogt (1957, cf. also Vogt 1959) for a cobalt amalgam and these are shown in fig. 6.9. The different diagrams refer to increasing ageing times; the resulting coercivities in oersted are as indicated and refer to measurements at 81°K. The fractions shown on the right of each diagram refer to those cobalt particles with size above about 0.02  $\mu$ . Figure 6.9 shows clearly how ageing leads to grain growth and increasing magnetic hardness.

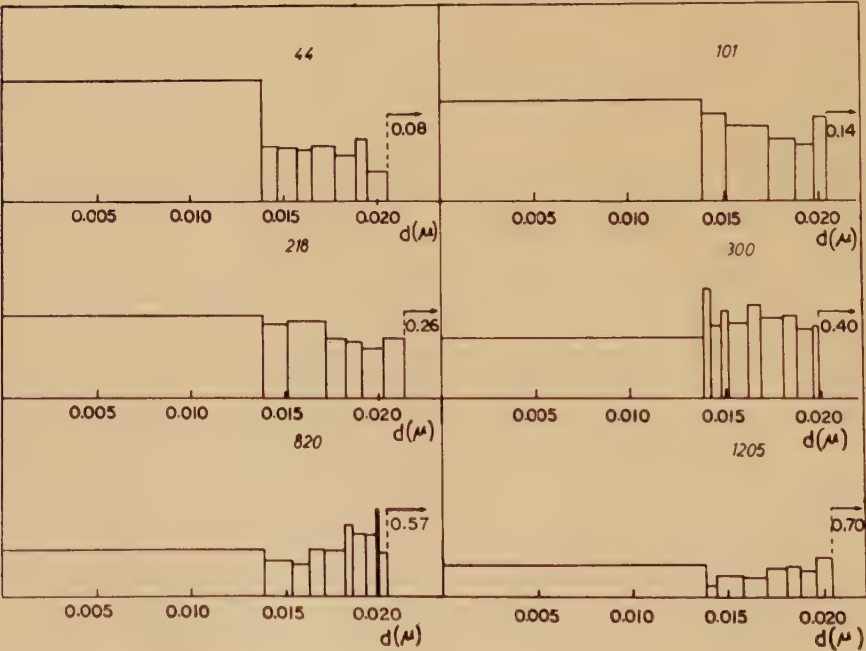
Another study of superparamagnetism in alloys has been reported by Hahn and Kneller (1958 a, b), who investigated partially ordered Ni-Mn alloys with 20-35% Mn, close to  $\text{Ni}_3\text{Mn}$ . As is well known (see for example, Bozorth 1951 b, p. 315), ordered  $\text{Ni}_3\text{Mn}$  is ferromagnetic while the disordered compound is non-magnetic with the curious properties described by Kouvel, Graham and Becker (1958), Kouvel *et al.* (1959), Kouvel and Graham (1959). As order is induced by means of an annealing treatment, ferromagnetic particles are formed embedded in the disordered non-magnetic matrix, and magnetic hardness is observed. For an alloy with 33% Mn, for example, heating for about 50 hours at 440°C raises the coercive force from very low values to about 430 oersted, a value which decreases on further heating. For alloys for which the ordering treatment has been carried to extremes, the coercivity, depending on the Mn content, reaches over 400 oersted. At the same time, the reduced remanence reaches a

Fig. 6.8



Size distribution for 1% Cu-Co.  $\phi(d)$ , distribution function ;  $d$ , diameter, microns. After Weil and Gruner (1956).

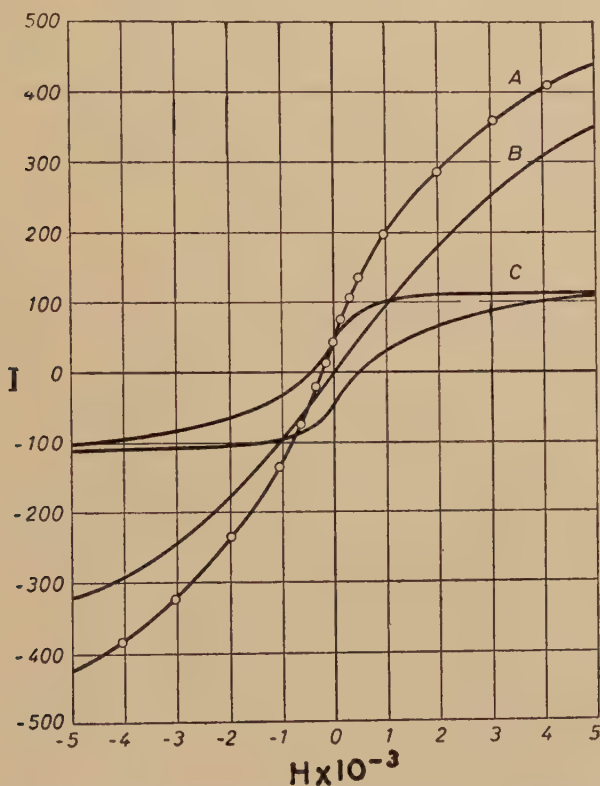
Fig. 6.9



Size distribution of 1.5% Hg-Co. For description, see text. After Henning and Vogt (1957).

maximum at about 25% Mn, but this maximum value is only about 0.3. Finally, saturation magnetization is very difficult to attain and is not yet reached in fields  $1.2 \times 10^4$  oersted. These results are interpreted in terms of the properties of mixtures of superparamagnetic and stable single domain particles. For an alloy with 29% Mn whose ordered phase consists entirely of superparamagnetic particles as a result of the appropriate heat treatment, Kneller estimates the mean sizes  $d_0$  and  $d_\infty$  from relations (6.2) and (6.3), obtaining the respective values  $0.0034\mu$  and  $0.0032\mu$ . This difference is ascribed to particle size variations, as in the earlier work of

Fig. 6.10



Hysteresis curves of partially ordered 29% Ni-Mn.  $I$ , magnetization, gauss,  $H$ , field, oersted. Curve A, observed curve at room temperature; B, estimated curve for superparamagnetic fraction of ordered  $\text{Ni}_3\text{Mn}$ ; C, estimated curve for stable single domain fraction. After Hahn and Kneller (1958 a).

Becker and others. Here a rectangular distribution is assumed, which gives agreement for the magnetization curve over the whole range of fields (see also Elmore 1938); the particles covered by this distribution range in diameter from  $0.0024\mu$  to  $0.0041\mu$ .



For alloys which have been so treated that finite remanence and coercive force is obtained, a fraction of the ordered phase is thermally stable, and the resulting measured hysteresis curve is the sum of these two components (see also Bean 1955). A curve for a 29% Mn alloy is shown in fig. 6.10, curve A. Here curve B corresponds to that for the superparamagnetic fraction of the particles, taken to be given by (6.1). Finally, by subtracting B from A, it was possible to estimate the curve C, corresponding to the stable single domain particles in the mixture, whose coercivity, 410 oersted at room temperature, is higher than the bulk coercivity of the whole mixture, 250 oersted. On lowering the temperature, the fraction of superparamagnetic particles decreases and the coercivity rises, to 570 oersted at 114°K for this specimen. This value is believed to arise as a result of slight shape anisotropy. By plastically deforming such alloys the bulk coercivity increases. This increase is small for alloys with less than 25% Mn but larger, with coercivities reaching over 700 oersted, for alloys with a higher Mn content. These changes are partly due to internal strain effects and partly to changes of the shape anisotropy of the ferromagnetic particles, as described earlier.

## § 7. ALNICO-TYPE PERMANENT MAGNET ALLOYS

### 7.1. *Introduction and Data up to about 1948*

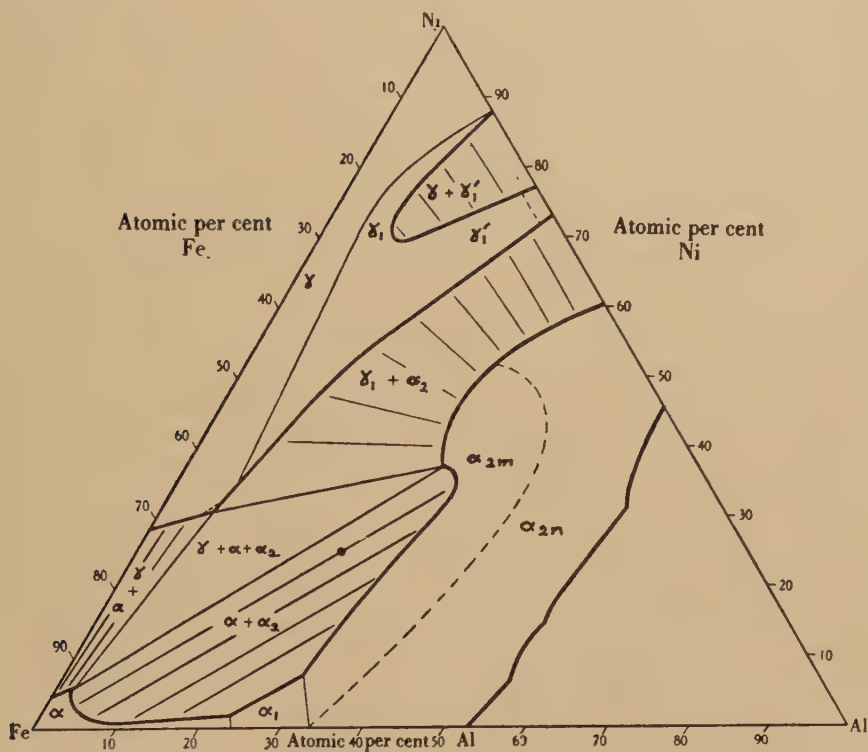
Permanent magnet alloys containing iron, nickel and aluminium were first produced by Mishima in 1931. Since then these alloys have been developed to such an extent that, in spite of the many other advances reported here, they remain pre-eminent among useful magnetically hard materials. Among these developments has been the addition, in varying quantities, of copper, cobalt, titanium, niobium, silicon, etc., the production of magnetic anisotropy by magnetic annealing treatments, and the preparation of magnet materials with aligned crystals. The resulting alloys have an enormously improved magnetic performance, for example a maximum energy product exceeding  $10^7$  gauss-oersted, but they are at the same time so complex metallurgically that the precise reasons for this performance are not at all clear.

Among early structural investigations on iron-nickel-aluminium alloys was that of Burgers and Snoek (1935). They applied a heat treatment, slow cooling from 1200° to 700°C at a controlled rate, to an alloy containing 28% Ni, 13% Al, and found that the coercivity rises to a maximum about 600 oersted as the cooling time increases, and then drops to lower values down to about 200 oersted as this time increases further. The state of optimum hardness was shown from x-ray studies to be one of incipient precipitation of what was thought from the existing phase diagram to be a f.c.c. phase in the b.c.c. matrix. The large coercivity was ascribed to coherency strains.

Köster's original phase diagram for the Fe-Ni-Al system was drastically amended by Bradley and Taylor (1938 a, b), and as a result the precipitation process had to be reconsidered. The new diagram is shown in fig. 7.1.

Here the Mishima alloy  $\text{Fe}_2\text{NiAl}$ , indicated in the  $\alpha + \alpha_2$  field, separates completely on slow cooling into an ordered phase in the  $\alpha_{2m}$  field and having composition  $\text{Fe}_6\text{Ni}_7\text{Al}_7$ , and a disordered phase in the  $\alpha$  field with composition  $\text{Fe}_{38}\text{NiAl}$ , i.e. almost pure iron. As in Burgers' and Snoek's work, the state of optimum magnetic hardness was that where the phase segregation was in an early stage. Small 'islands' of the iron-rich  $\alpha$  phase were envisaged to be formed in the  $\alpha_{2m}$  matrix but still to be partly coherent with it. Snoek (1938, 1939) obtained evidence on the heterogeneity of these alloys

Fig. 7.1



Ternary diagram for Fe-Ni-Al.  $\alpha$ , disordered b.c.c. phase;  $\alpha_1$ , ordered b.c.c. with  $\text{Fe}_3\text{Al}$  structure;  $\alpha_2$ , ordered b.c.c. with  $\text{FeAl}$  or  $\text{NiAl}$  structure;  $\alpha_{2m}$ , magnetic  $\alpha_2$  phase;  $\alpha_{2n}$ , non-magnetic  $\alpha_2$  phase;  $\gamma$ , disordered f.c.c. phase;  $\gamma_1$ , ordered f.c.c. with  $\text{Ni}_3\text{Al}$  or  $\text{Ni}_3\text{Fe}$  structure; dot,  $\text{Fe}_2\text{NiAl}$ . After Bradley and Taylor (1938 a, b), with change of notation.

from measurements of the internal demagnetization coefficient. He concluded that the phase boundary of the  $\alpha + \alpha_2$  field extends much further than shown in fig. 7.1, and that in the magnetically hard state there are few non-magnetic 'air gaps', both  $\alpha$  and  $\alpha_2$  being here magnetic phases. Sucksmith (1939) obtained evidence about the segregation process and the

properties of the phases from measurements of the magnetization, temperature curves of the single phase and two-phase  $\text{Fe}_2\text{NiAl}$  alloy. The last was formed by quenching from  $800^\circ\text{C}$ , and the magnetization curve showed a pronounced dip at  $450^\circ\text{C}$ , evidence for two phases. Sucksmith found that the segregation is according to



and that the saturation moments of the phases are 212 and 61 e.m.u.  $\text{g}^{-1}$ . According to this experiment even the  $\alpha_{2m}$  phase is thus quite strongly magnetic.

Kiuti (1941) reported results of measurements on  $\text{Fe}_2\text{NiAl}$  agreeing generally with those of Bradley and Taylor. The two phases present in the optimum state were both shown to be b.c.c. in structure; any f.c.c. phases which may be formed were present in only small amounts at the surfaces of the specimens and were unstable, being removable by annealing. Kiuti also gave a series of microstructure photographs, showing well defined relatively large precipitates with apparently elongated shape. These were presumably only observable by optical microscopy for alloys beyond the state of optimum magnetic hardness.

Full details on the optimum composition and heat treatment of these isotropic alloys have been given, among others, by Betteridge (1939). He investigated the critical quenching temperature, cooling rate and tempering time and temperature for Fe-Ni-Al alloys of varying composition. Optimum maximum energy product was obtained for an alloy with 26.7% Ni and 12.9% Al, quenched in water from a single phase condition at  $1100^\circ\text{C}$  at  $28^\circ\text{Csec}^{-1}$ , and then tempered for 4 hours at  $650^\circ\text{C}$  where incipient phase segregation takes place. This treatment was found to give  $H_c = 518$  oersted and  $(BH)_{\max} = 1.35 \times 10^6$  gauss-oersted. The coercive force depends very critically on the Al content, the remanence more on the Ni content. Carbon impurities even as low as 0.1% impair all these quantities. Betteridge also investigated the effect of adding copper on the properties of these alloys; he found that with 3.5% Cu a  $(BH)_{\max} = 1.5 \times 10^6$  gauss-oersted was attained by quenching from above  $950^\circ\text{C}$  and tempering at  $550^\circ\text{C}$ . He also investigated the effects of cobalt additions; an alloy with 23% Ni, 10% Al, 10% Co and 5% Cu, quenched from the much higher temperature  $1300^\circ\text{C}$  and tempered at  $650^\circ\text{C}$ , had the highest energy product  $1.8 \times 10^6$  gauss-oersted. Full details of the preparation and properties of commercial isotropic alloys are tabulated by Edwards (1957).

The greatest advance in the technology of Alnico-type permanent magnet alloys was the discovery of the magnetic annealing effect, leading to a material with anisotropic magnetic properties. Oliver and Shedden (1938) cooled an alloy with 18% Ni, 10% Al, 12% Co, 6% Cu in a field 4400 oersted from  $1200^\circ\text{C}$ . The anisotropy produced was a 20% increase in  $(BH)_{\max}$  in the field direction and a 10% reduction perpendicular to it. This anisotropy was due entirely to changes in the remanence and fullness



factor, as the coercive force remained isotropic. It is sad to relate that the developments of this important achievement were thereafter allowed to pass abroad. Jonas and Meerkamp van Embden (1941) heat treated an alloy with 14% Ni, 8.5% Al, 23% Co and 3% Cu in a field 3000 oersted. The maximum energy product parallel to the field direction was  $5.2 \times 10^6$  gauss-oersted, perpendicular to it only  $0.7 \times 10^6$  and for the corresponding isotropic alloy  $2.2 \times 10^6$ . The corresponding values of coercive force were about 650, 410, and 580 oersted, and for the remanent induction about  $1.2 \times 10^4$ ,  $0.4 \times 10^4$  and  $0.9 \times 10^4$  gauss. The fullness factor of the annealed magnet had the high value 0.76 in the preferred direction. Subsequent to this achievement structural investigations aimed at an understanding of the causes of the magnetic anisotropy which, it was hoped, would lead to even greater improvements.

Among a number of investigations in the period up to 1948 were those of Jellinghaus (1943, 1948), Zumbusch (1942) and Oliver and Goldschmidt (1946). Jellinghaus (1943) investigated alloys with 15% Ni, 5.7 to 16.6% Al, 23% Co, 3% Cu. A f.c.c.  $\gamma$  phase was detected only for the lowest Al contents, and it was found to be absent above about 6%; here the whole material seemed to have a b.c.c. structure, and an ordered  $\alpha$  phase was detected at the higher Al contents. The magnetic properties of these alloys were found to be favourable for only a very narrow range of Al contents, about 8–9%, where coercivity, remanence and maximum energy product are all high. Zumbusch (1942) investigated these anisotropic alloys over a wider range of compositions, including as a further component up to about 4% Ti. He found that the best permanent magnet alloys of this type contain 14–15.5% Ni, 7.8–9.2% Al, 21.5–23.5% Co, 3–4% Cu and less than 1% Ti. These compositions have been used since in some, but not all, commercial materials (see Edwards 1957). The heat treatment recommended by Zumbusch consists of cooling from 1250°C at about  $1^\circ\text{Csec}^{-1}$  to 500°C in a field well above  $2 \times 10^3$  oersted, followed by tempering for 10 hours at 550°C.

Anisotropic permanent magnets have also been prepared by powder metallurgical sintering techniques (see, for example, Garvin 1947, Anon 1957 a), causing usually little change in coercivity, but, due to the density decrease, a drop in remanence and hence maximum energy product compared with cast alloys. For Alcomax II, for example, Garvin quotes a drop from 4.3 to  $3.3 \times 10^6$  gauss-oersted.

An extensive x-ray investigation on anisotropic permanent alloys has been reported by Oliver and Goldschmidt (1946), whose results, of a 'bewildering complexity', cannot all be quoted here. It was found that above about 1270°C the alloys investigated, including some in the range of commercial anisotropic materials and some outside this range, have a b.c.c. structure which is ordered as FeAl and thus corresponds to  $\alpha_2$  in fig. 7.1 (Oliver calls it  $\beta$ ). This phase can be preserved by sufficiently rapid cooling. Tempering this quenched single-phase material at 580°C causes incipient precipitation of another b.c.c. phase, here called  $\beta'$ ,

which also has a superlattice and a larger lattice constant than the high temperature phase. The precipitation at this temperature is only on an atomic scale, being characterized by the appearance of 'side bands' on the x-ray lines, as in Cu-Ni-Fe alloys (cf. § 8), which point to a periodic modulation of the lattice structure of the high temperature phase. The precipitation of the new phase is made more complete by tempering at a higher temperature about 650°C to 800°C. By applying an annealing treatment over a wide range of temperatures, a reversible transformation to a f.c.c. phase (here called  $\alpha$ ) may be brought about, as well as to a third b.c.c. phase  $\beta''$  of lower lattice constant than  $\beta$ . The f.c.c. phase occasionally exhibits order as the  $\gamma_1$  phase of fig. 7.1. On quenching from about 1200° it was found that the  $\beta$  phase may suffer tetragonal distortion. This temperature lies in the range of stability of the f.c.c.  $\alpha$  phase (980°–1220°C), which is thus bound above and below by stable body centred phases as in carbon steels. Annealing in this range causes the  $\alpha$  phase to grow in volume and then to decay again as the time of heating increases, finally ending up with a pure b.c.c.  $\beta(\beta'')$  phase. Although 580°C is well below the range of stability of the f.c.c.  $\alpha$  phase, it may still be formed there in a metastable form, which may tend to reduce strains. This phenomenon is regarded as important, as it takes place at temperatures close to those used in the preparation of the optimum permanent magnet alloys. Oliver and Goldschmidt also investigated the effects of the magnetic heat treatment on the distribution and proportions of all these phases, and observed that these took up preferred orientations. The maximum effect of the orienting field occurred if a proportion of the f.c.c. phase was present as this, being not always very stable, is sensitive to external influences. The phase relations are here much more complex than in Fe-Ni-Al alloys, but it is, nevertheless, to some extent possible to correlate the results of Oliver and Goldschmidt's work with Bradley and Taylor's phase diagram, fig. 7.1. The important new result seems to be that f.c.c. phases also have a pronounced effect on the magnetic properties of these alloys, foreshadowing the later work of Koch, v.d. Steeg and de Vos (1957, see below).

### 7.2. *Data after 1948: General Remark*

About this time it began to be realized that the magnetic hardness of Alnico-type materials might be due not so much to classical strain effects as to the properties of the precipitated phases themselves if these are present in a finely divided form. Since then a vast body of publication, of which only a part is discussed in what follows, has been concerned with investigations of the nature of these precipitates and with the causes of the magnetic anisotropy. These investigations have been of various kinds, magnetic, structural, etc., but in reviewing them it is difficult to bring about a clear-cut separation into well defined areas of study.

It is well to stress again that an interpretation of the magnetic hardness and anisotropy based solely on rotational effects in single domain precipitate particles is by no means firmly established. Some authorities, for example

Geisler (1953), favour, with considerable justification, an interpretation based on coherency strains. No doubt the correct interpretation in any one case contains elements of both as well as other philosophies.

### 7.3. Structural Investigations

Bradley (1949a, b, 1951, 1952) re-investigated the phase diagram of Fe-Ni-Al and found considerable complications over fig. 7.1 in the f.c.c. fields. He also obtained microscopical evidence as to the nature of the precipitation in the b.c.c. field of optimum magnetic hardness. The precipitates may be either disordered, such as  $\alpha$  of fig. 7.1, or ordered, such as  $\alpha_2$ , depending on their relative amounts. Depending on circumstances, the precipitates may be spherical, cubical or plate-like; the cubical precipitates of the ordered phase were found to be integral multiples of a mosaic unit about  $0.25\mu$  in size. From these the iron-rich  $\alpha$  phase is formed first by precipitation at the cube corners, and then by growth to form eventually a continuous network or maze. This result foreshadows that of Kronenberg and Tenzer (1958), discussed below.

If both phases are present in approximately equal proportions they were found by Bradley to form laminated structures alternatively iron and Ni-Al rich, but with no clear-cut boundary. The lamellae are tetragonally distorted, and give rise to an x-ray side band structure of the type previously observed by Burgers and Snoek (1935) and Oliver and Goldschmidt (1946). Relative decreases of one or other of these phases leads to an eventual break-up of the lamellae, tending to the type of structure discussed above.

Geisler (1951b) obtained optical microscope photographs of an anisotropic alloy, Alnico V, for which precipitation (Geisler 1950) takes place of plate-like particles of the iron-rich phase parallel to some but not all of the (100) planes of the matrix. Geisler found that this anisotropy is produced even if no field was applied during the precipitation process, due to the orienting effects of internal fields. This internally produced anisotropy should be manifested by a high remanence.

A great advance in the structural investigations of these materials came with the application of electron microscopy. The first experiments seem to have been carried out independently in two places. Skakov (1951) investigated  $\text{Fe}_2\text{NiAl}$  alloys quenched from solid solution and then tempered. The iron-rich precipitates,  $\alpha$  phase of fig. 7.1, appeared as platelets, about  $0.1\mu$  long and  $0.01\mu$  wide, on the cube faces of the NiAl rich matrix after a short anneal at  $750^\circ\text{C}$ ; the thickness of the platelets increased and the coercivity dropped after a longer anneal at a higher temperature. The ordered phase,  $\alpha_2$  of fig. 7.1, is distorted during the heat treatment, possibly giving rise to coherency strains. Later Russian work on these alloys (Ivanov 1951, Ivanov and Kazimirov 1951, Ivanov *et al.* 1951) also suggested that the iron-rich phase precipitates as platelets and, in general agreement with Bradley (1949b), that, if precipitation of the NiAl rich phase takes place, the particles come down as spheroids. It was also suggested, in agreement with Oliver and Goldschmidt (1946), that



added elements may stabilize the f.c.c. phase in the Fe-Ni-Al system. Among more recent electron microscopical and related investigations from Russia is the work of Lifshitz and Lvov (1957).

A more detailed combined electron microscope and electron diffraction study on a single crystal of the anisotropic alloy Alnico V (for compositions of this and other alloys referred to, see Edwards 1957) was reported by Nesbitt and Heidenreich (1952 a, b). They found that the heat treatment produced precipitates in the shape of rods of dimensions about  $0.01 \times 0.01 \times 0.04 \mu$  which coalesce into platelets about  $0.02 \mu$  apart. The precipitates were found to be cobalt rich and to have a f.c.c. structure with a lattice constant about 10A.U.; this structure was believed to be metastable. The precipitates were found to be aligned with their [100] directions parallel to the same direction of the matrix; magnetic alignment is then most effective if the field is also parallel to a [100] direction. One major deficiency in this work was that the observations could, in part, only be carried out for specimens in a state of low coercivity, produced by annealing at  $800^\circ\text{C}$ , since only then were the precipitates large enough for observation; the subsequent extrapolation to the optimum state may not always be entirely reliable.

Kronenberg (1954) was later able to detect electron microscopically the precipitates even in the optimum state, but he also could not obtain sufficient detail without applying the  $800^\circ\text{C}$  heat treatment used by Nesbitt and Heidenreich and producing precipitate growth and loss of coercivity. Fahlenbrach (1954, 1955, 1956) used more refined electron microscopical techniques and was able to obtain useful electron microscope pictures for Alnico-type material with coercivity 650 oersted. The precipitates were observed to be needle shaped with estimated dimensions  $0.04 \times 0.04 \times 0.1 \mu$ , larger than Nesbitt's value. A tentative chemical separation of the phases also enabled Fahlenbrach to estimate their individual properties, and he found that for the 'precipitates' and 'matrix' the saturation inductions had the respective values  $1.3 \times 10^4$  and  $1.5 \times 10^4$  gauss and the Curie temperatures  $750^\circ$  and  $860^\circ\text{C}$ , the last being equal to that of the alloy itself.

One of the most extensive investigations has been reported by Schulze (1956) on anisotropic Alnico with parallel coercivity about 600 oersted. A statistical analysis gave for the dimensions of the precipitate particles the average values  $0.034 \times 0.038 \times 0.12 \mu$ , a dimensional ratio about 3. The mean distance between particles was estimated as  $0.004 \mu$ , the number of particles per  $\mu^3$  as  $5 \times 10^3$  and their volume fraction as 63%. The dimensions agree well with Fahlenbrach's. Schulze also investigated the influence on the precipitates of grain boundaries, and observed that in some cases the aligning field could cause particle orientation across one or even two boundaries, with only slight disturbances in their immediate neighbourhood. In other cases marked misalignments were observed and ascribed to crystal anisotropy effects.

The most impressive results were obtained by Haanstra *et al.* (1957) and de Jong *et al.* (1958). They investigated single crystals or coarse grained

crystal oriented specimens of Ticonal G, Ticonal X and Ticonal XX whose [100] directions are parallel to the orienting field. Almost perfect alignment was observed of elongated particles in a (100) plane parallel to the field direction, but perpendicular to this direction the particles show no marked elongation or alignment. For Ticonal G the dimensions were about  $0.03 \times 0.03 \times 0.012 \mu$ , close to the earlier values. For Ticonal XX, with  $H_c = 1315$  oersted, reduced remanence  $j_r = 0.96$  and  $(BH)_{\max} = 11 \times 10^6$  gauss-oersted, similar results were obtained, but the texture is more pronounced, the width of the particles smaller (about  $0.02 \mu$ ), the dimensional ratio higher and the particle distribution more regular. The actual results are shown in fig. 7.2 (Pl. 4, 5). Unfortunately, as these authors wisely point out, these pictures do not show conclusively whether actual precipitation of a second phase is demonstrated, or whether merely periodic fluctuations in concentration are shown up by a differential sensitivity to the etchant; such fluctuations would also lead to the x-ray 'side bands' which have frequently been observed (see above).

#### 7.4. Domain Patterns

The earliest Bitter patterns on an Alnico-type material seem to have been those of Nesbitt and Williams (1950). When Alnico V was heat treated so as to be magnetically soft, pronounced patterns were observed and the domains contracted in width, with a rotation of the magnetization, as the magnetization increases. At saturation the domain walls had quite disappeared and the magnetization was parallel to the direction of the cooling field. After optimum heat treatment ( $H_c = 600$  oersted) no domain patterns were visible at the remanence point, but small spike-like domains were found to appear and grow on demagnetization. It was suggested that these spikes were oriented precipitate particle aggregates. Further Bitter pattern investigations on soft '800°C' Alnico V by Nesbitt and Williams were reported by Bozorth (1951a, see also Nesbitt 1950). Here long domains aligned parallel to the cooling field were found to cross crystal grain boundaries with little distortion, a result to be compared with that obtained by Schulze (1956). The magnetization was found to be parallel to the cooling field rather than the easy direction of magnetization nearest to this field (see discussion below). On applying a magnetic field parallel to the direction of the cooling field, the domain walls were observed to move and the hysteresis loop to be square.

Bates and Martin (1955, see also Bates 1955) reported results on some Alnico specimens with coercivities up to 100 oersted. For the softer specimens domain patterns similar to those of Nesbitt and Williams were observed and boundary motions found to take place during magnetization by a field parallel to the 180° walls. For the harder specimens the domain boundaries lost some of their straightness, tending, no doubt, to Nesbitt's spike-like patterns. Bates and Davies (see Bates 1955) also reported some results on crystal oriented Columax.

Kussmann and Wollenberger (1956) also investigated an Alnico material with coercive force 670 oersted. They observed powder patterns, having the form of lines running parallel to the orienting and magnetizing fields,

during demagnetization beyond the remanence point. As with Nesbitt and Williams (1950) it was tentatively suggested that these lines are really magnetically coherent regions consisting of smaller oriented particles. This work was later continued by Andrä (1956 b), who found, apart from results in line with earlier ones, that nucleation of spike-like domains similar to those of Nesbitt and Williams frequently takes place at grain boundaries and imperfections.

The apparently inconclusive results of these various investigations, which at first sight do not seem to correlate very closely with the structural investigations discussed earlier, have been extended in a preliminary but more satisfactory way by Kronenberg and Tenzer (1958). They were able to spread their colloid on the surface of a polished Alnico V specimen, and, after it had dried, to lift it off the surface by coating with a collodion film which was then studied electron-microscopically. A structure with orientation close to that of the magnet and with particle size of the order of that revealed by the earlier structural investigations was observed. The precipitates show up as elongated and, after the optimum heat treatment, as forming a complete anisotropic network separating particles of the 'matrix'. A series of photographs, reproduced from Kronenberg and Tenzer's paper, is shown in fig. 7.3 (Pl. 6). These pictures apparently show up in fine detail the structure which is inherent in the earlier Bitter patterns but could not be resolved there. The authors believe that over the flat portion of the demagnetizing curve of fully treated Alnico V the matrix, having a lower saturation magnetization, is demagnetized by reversals; close to the coercive force the more strongly magnetic precipitates also begin to reverse, this reversal being nucleated at matrix particles and then spreading throughout the network of precipitates. This process causes the attraction of the surface for the colloid to lessen in those parts where the reversals have already taken place. Hence the colloid particles agglomerate, and would then form the spikes, lines, etc. exhibited as a 'domain structure' by the earlier investigations near the coercive force point.

### 7.5. *Magnetostriction and Anisotropy*

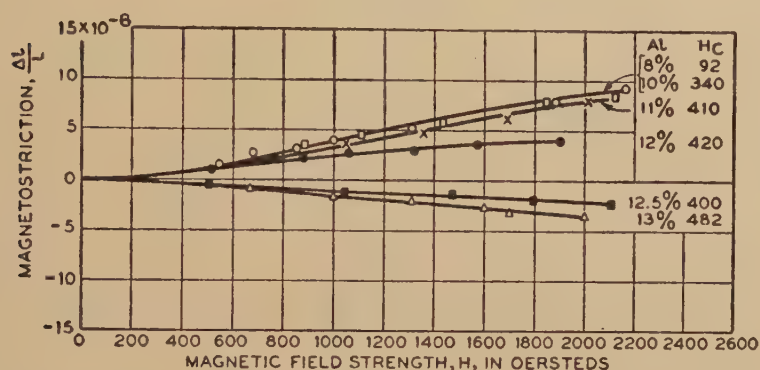
Some information on the process of precipitation, leading to magnetic hardness and anisotropy, has been gained from the observations just described. Magnetic properties, such as magnetostriction and anisotropy, have also been extensively studied in an effort to interpret the observed behaviour of Alnico-type materials.

Hoselitz and McCaig (1949 a) measured the magnetostriction of the alloy Alcomax II, an anisotropic material (cf. Edwards 1957). By carrying out measurement parallel and perpendicular to the preferred orientation, they concluded that in the remanent state the domain magnetization in each crystal grain is along that cube edge which is closest to the direction of the aligning field. The reduced remanence  $j_r^H$  was measured as 0.87, dropping to 0.81 after tempering at 550° to 700°C, showing that the alignment had been impaired to a slight extent, although the coercive force



increases. The immediate application of these ideas was in the development of a material Columax for which the cube edges of the crystal grains were aligned as far as possible. Magnetostriction and remanence measurements for this material were reported by McCaig (1949). The measurements were for a specimen for which the preferred direction and the common [100] axis were parallel, and for one for which they were perpendicular. Calculated  $j_r''$  values are 1 and 0.9 respectively, while measurement gave 0.94 and 0.93 in the two cases. The measured magnetostriction constants for various crystal directions could all be fitted approximately by two coefficients  $\lambda_{100} = 36.4 \times 10^{-6}$ ,  $\lambda_{111} = 7.8 \times 10^{-6}$ . The technical properties of crystal oriented permanent magnet alloys show a remarkable improvement over materials with random crystals, as described below.

Fig. 7.4



Magnetostriction coefficient of Fe-Ni-Al alloys. After Nesbitt (1950).

Hoselitz and McCaig (1949 b, see also Hoselitz 1950) later made a more detailed analysis on the basis of measurements of the approach to saturation of the technical magnetization. This enabled an effective cubic crystal anisotropy coefficient to be derived, the value for isotropic Columax being  $2 \times 10^6 \text{ erg cm}^{-3}$ . From the measured value of the r.m.s. spontaneous magnetization for the heterogeneous material the coercivity could then be estimated from a formula of Néel (1946), and was found to agree with observation. For anisotropic Columax the results are interpreted in terms of an additional effective uniaxial anisotropy coefficient of value somewhat less than that of the cubic coefficient. The uniaxial term is interpreted on the basis of shape anisotropy effects.

A very extensive series of magnetostriction measurements on Alnico-type and other permanent magnet alloys was reported by Nesbitt (1950). For Alnico V and related alloys the polycrystalline magnetostriction coefficients  $\lambda$  were found to vary greatly with the heat treatment, and values ranging from  $2$  to  $43 \times 10^{-6}$  were observed. Some interesting results were obtained for the simpler Fe-Ni-Al alloys with Al contents

from 8 to 13% and Ni content 29%. As shown in fig. 7.4, which refers to alloys cooled from 1300–1350°C at 2–5 deg sec<sup>-1</sup>, the magnetostriction of an alloy with about 12.5% Al is zero, although the coercivity is as much as 400 oersted. This result was taken to mean that the classical strain theory of coercivity is inapplicable for these materials. It does not seem entirely conclusive, however, that it also excludes interpretations based on the effects of localized coherency strains where bulk magnetostriction coefficient may not be so significant.

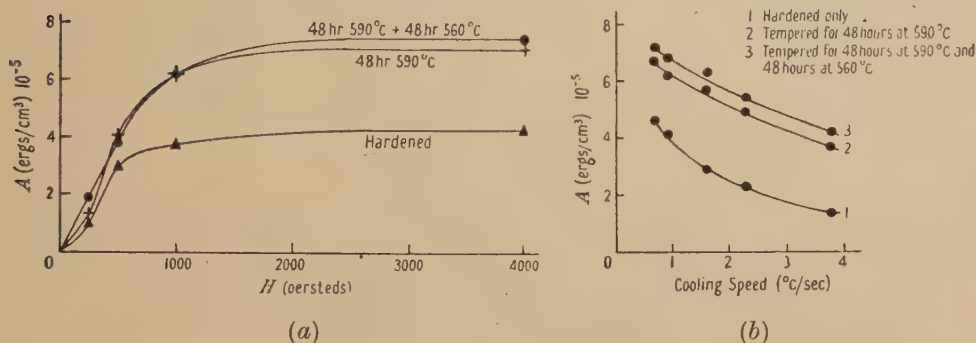
Parallel to these measurements there has also been a series of investigations of the crystal anisotropy by means of torque curve measurements. Hoselitz and McCaig (1951) investigated a Columax specimen which had been either quenched or cooled slowly without a field, or cooled in a field parallel to the columnar axis. In the first two cases an effective cubic anisotropy was developed having respectively positive and negative values. After the magnetic treatment a uniaxial anisotropy coefficient about  $1.2 \times 10^6$  erg cm<sup>-3</sup> was developed. When the cooling field was applied at some angle (22.5°) to the columnar axis, the preferred direction was found to be at an angle less than 5° with this axis, and over 18° with the field direction; this result is in line with the earlier magnetostriction measurements. Hoselitz and McCaig (1952) extended these investigations to Alcomax III specimens, both random and columnar, which had been heat treated in different ways. An effective uniaxial anisotropy coefficient  $A$  was derived from the measurements, and its variation with orienting field strength and cooling speed is shown in fig. 7.5; the optimum treatment for this material is also indicated. Maximum coercivity, about 650 oersted, is reached for  $A$  about  $0.7 \times 10^6$  erg cm<sup>-3</sup>, i.e. after cooling in fields about  $2 \times 10^3$  oersted at about 1°C sec<sup>-1</sup>. Similar measurements were also reported for other alloys; for Alcomax IV optimum treatment gave  $A = 1.1 \times 10^6$  erg cm<sup>-3</sup>. Using the anisotropy data it was possible to estimate the perpendicular initial susceptibility for rotational processes, giving 0.59 for optimum Alcomax IV, compared with a measured value 0.64.

The question as to whether the easy direction of magnetization in each crystal of an anisotropic permanent magnet material is along the [100] direction nearest to the orienting field direction or to this direction itself was further investigated on columnar Alcomax III by McCaig (1953), after doubt had been thrown on the former hypothesis (see below). For normal cooling rates, 1.4°C sec<sup>-1</sup> (see fig. 7.5), and not too large angles between crystal and field directions, the easy directions were found to be close to the columnar axis, but for larger angles, faster cooling rates and unfavourable heat treatments the easy directions may be closer to the field direction, the values of  $A$  then being smaller.

Another extensive series of investigations has been reported by Nesbitt and associates. Nesbitt and Heidenreich (1952a, b) supplemented their electron microscope studies by torque measurements on a single crystal disc of Alnico V, heat treated either with or without the application of an

aligning field in various directions. The largest value of the anisotropy constant was reached if the field is applied parallel to a [100] direction in a (100) plane; this value was  $0.96 \times 10^6 \text{ erg cm}^{-3}$  and the resulting coercive forces  $H_c^{\parallel} = 600$  oersted,  $H_c^{\perp} = 220$  oersted. The heat treatment (cooling from  $1300^\circ\text{C}$  at  $2^\circ\text{C sec}^{-1}$  and tempering for 7 hours at  $590^\circ\text{C}$  in the optimum state) was suggested to align the precipitates in a [100] direction, the precipitates being plates of metastable cobalt rich f.c.c. rod-like elements, separating a larger volume of rod-like elements of the matrix. The observed bulk coercive force was shown to be reasonably accounted for by the crystal anisotropy of the matrix and precipitate particles and the shape anisotropy of the matrix, the sizes involved, precipitate rods  $0.01 \times 0.01 \times 0.04 \mu$ , separating matrix rods of width  $0.02 \mu$ , being of the right order for single domain rotational processes to take place.

Fig. 7.5



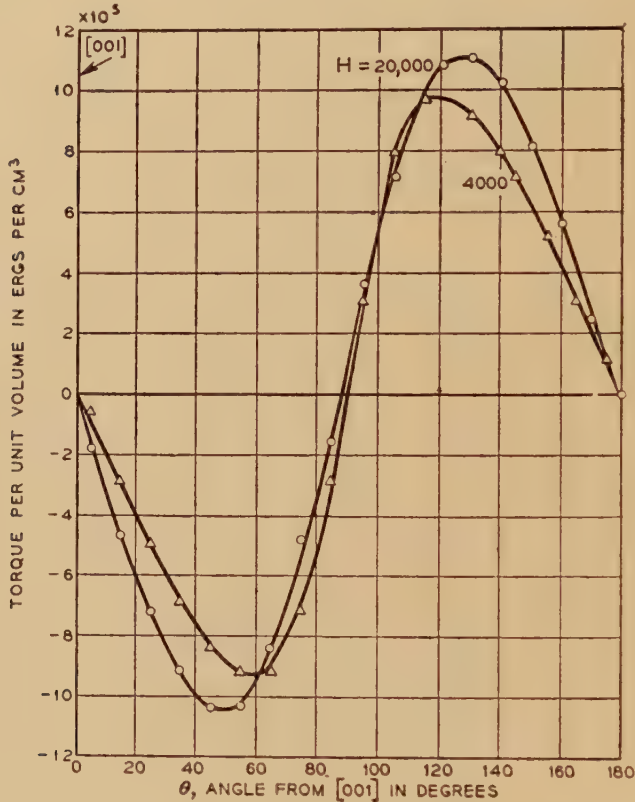
Effective uniaxial anisotropy coefficient of Alcomax III. (a)  $A$  as a function of orienting field strength; (b) as a function of cooling speed. After Hoselitz and McCaig (1952).

Nesbitt and Heidenreich (1953) investigated the torque curves of the simpler  $\text{Fe}_2\text{NiAl}$  alloys. Here again the electron diffraction evidence was that the precipitates had a f.c.c. structure with spacing  $10 \text{ \AA}$ ; this result seems to contradict those shown in fig. 7.1. The anisotropy constant was found to be negative in the optimum state, the easy axis of magnetization of the precipitate crystals being [110]. This work on  $\text{Fe}_2\text{NiAl}$  was extended by Nesbitt, Williams and Bozorth (1954), which clarified the earlier interpretations. The torque curves were analyzed in terms of precipitated plate-like rod-constituted particles oriented in three perpendicular directions, giving [111] as the easy direction of magnetization in low fields ( $< 7 \times 10^3$  oersted). The torque curves of Nesbitt and Heidenreich (1953) are thus more sensibly interpreted in terms of shape anisotropy rather than apparent crystal anisotropy effects. Measurements in higher fields ( $> 1.2 \times 10^4$  oersted) show that here the torque has suffered a reversal in sign. Here the effect of shape anisotropy, in the above sense, diminishes, and the observed anisotropy is now due to the crystal effects, the easy



directions being [100]. The torque reversals were absent at high temperatures, 600°C, where the crystal was found to be isotropic. At low field strengths the [111] easy directions re-appeared in a (110) plane. By extrapolation from 600°C, the contribution, due to shape anisotropy, to the bulk coercive force was shown to be about 75% of the total.

Fig. 7.6



Torque curves for Alnico V. After Nesbitt and Williams (1955).

Similar measurements on Alnico V were later reported by Nesbitt and Williams (1955). Here no torque reversals were observed at high fields, the torque maxima tending to zero. Hence it was concluded that crystal anisotropy effects are negligible. For a magnetically heat treated (110) disc specimen with the aligning field parallel to [100], the anisotropy, due entirely to shape, is uniaxial, as shown in fig. 7.6, and has a value  $1.08 \times 10^6$  erg  $\text{cm}^{-3}$  at the highest field. The corresponding coercive force, 1960 oersted, is, however, much higher than the 715 oersted observed. This is ascribed to the fact that during the torque measurements the magnetization vectors rotate out of the plane of the plate-like rod-constituted precipitate

particles, while during coercivity measurements they rotate in the planes, which is easier. When both processes are arranged to be similar, the calculated and observed coercivities are more nearly equal.

These measurements were carried out in the light of a 'theory' of magnetic hardness and anisotropy proposed earlier by Kittel, Nesbitt and Shockley (1950, see also Geisler 1951a, b, Hoselitz and McCaig 1950, Goldman and Smoluchowski 1950, Kittel and Galt 1956). They noted that during the magnetic heat treatment of Alnico V the orienting field is effective during cooling in the range  $900^{\circ}$  to  $800^{\circ}\text{C}$ , and that quenching from  $800^{\circ}\text{C}$  causes the specimen to be already anisotropic though still magnetically soft. They hence suggested that in this range of temperatures thermal nucleation of plate-like precipitates takes place, the plates being oriented anisotropically so as to minimize their demagnetizing energy in the orienting field. The increase of magnetic hardness during the subsequent tempering at  $600^{\circ}\text{C}$  was suggested to be a result of the growth of the precipitates on the planes on which nucleation had earlier taken place. The hypothesis that the anisotropy is developed chiefly during nucleation rather than the growth of precipitates has been verified experimentally by Nesbitt and Williams (1957). Almost completely standard Alnico V properties were attained if the orienting field is on only during cooling over the narrow range  $840^{\circ}$  to  $790^{\circ}\text{C}$ , where the nucleation and orientation takes place, growth occurring during the subsequent tempering at  $600^{\circ}\text{C}$  without a field. If the field is on only below  $790^{\circ}\text{C}$  the maximum energy product is less than half that of the fully treated specimen, so that nucleation seems to have been almost completed before the field was ever applied and able to cause orientation. If the specimen is cooled to  $790^{\circ}\text{C}$ , the field switched off and slow cooling continued, the maximum energy product also dropped compared to its value attained after quenching from  $790^{\circ}\text{C}$ . This drop is presumably a result of the partial destruction of the anisotropy by thermal fluctuations.

The most effective range for nucleation and alignment is thus  $840^{\circ}$  to  $790^{\circ}\text{C}$ , the lower limit being particularly critical. The nucleation may be regarded as an activation-diffusion process, with an activation energy  $70\text{ kcal mol}^{-1}$ .

Torque curve measurements on Alnico V and VII have also been reported by Jacobs (1957) who derived the rotational hysteresis and the integral  $R$  defined by relation (2.11). Values of  $R$  were found to be in the range 1.0 to 1.5, implying that the rotational processes in precipitates are not purely coherent (cf. § 2).

The observations discussed so far show how difficult it is to gain a clear understanding of all the problems raised. Magnetic hardness and anisotropy seems to arise as a result of the presence of at least two phases, both magnetic but of uncertain individual properties such as structure, magnetic moment, composition, relative amount and degree of definiteness and intergrowth. Although the phases are apparently present in a finely divided form in the state of optimum hardness, so that at first sight single domain

effects probably play some part, the physical set-up is so complex that a full quantitative explanation, say of the magnitude of the coercive force after a certain heat treatment, will probably never be possible. Nevertheless, certain guiding principles seem to have emerged, and these may be both applied in further improvements of the technical properties of Alnico-type materials, and also strengthened by further fundamental investigations related to those already described.

### 7.6. *Effects of Structure on Technical Properties*

The fact that in the magnetic annealing treatment of these alloys the aligning field is most effective in producing optimum properties if it is applied parallel to a [100] direction led to the development about 1949 of polycrystalline materials with aligned columnar crystals. The aim was to produce a useful material approaching in its susceptibility to magnetic alignment as closely as possible that of a single crystal. Koch and de Vos (1954) found that casting the alloys by means of the lost-wax method is most efficient. The mould is fired at a very high temperature and then cast after being placed on a chill plate, causing the growth of well aligned columnar crystals. The properties of crystal oriented Ticonal GG are given by Meerkamp van Embden (1957) as  $H_c = 720$  oersted,  $B_r = 1.45 \times 10^4$  gauss,  $(BH)_{\max} = 8.3 \times 10^6$  gauss-oersted. These values compare favourably with those of a single crystal of Ticonal G, for which Zijlstra (1956) gives  $(BH)_{\max} = 7.6 \times 10^6$  gauss-oersted in the [100] direction, and Koch, v.d. Steeg and de Vos (1957)  $H_c = 730$  oersted,  $B_r = 1.40 \times 10^4$  gauss,  $(BH)_{\max} = 8.0 \times 10^6$  gauss-oersted. In England two types of material were produced about the same time, namely semi-columnar Alcomax S.C. with  $(BH)_{\max} = 5.8 \times 10^6$  gauss-oersted, and fully columnar Columax, stated to have been prepared by grinding away unfavourably oriented crystals. For this material Anon (1952) gives  $H_c = 840$  oersted,  $B_r = 1.34 \times 10^4$  gauss,  $(BH)_{\max} = 8.63 \times 10^6$  gauss-oersted.

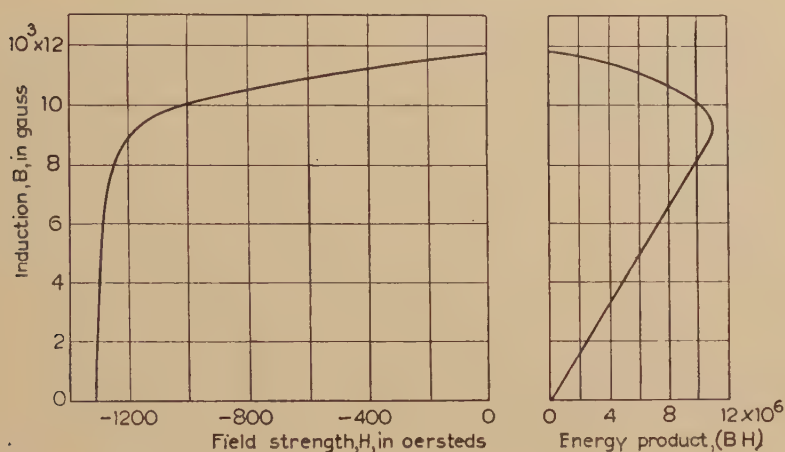
The process of crystal orientation in Ti containing Ticonal X is much more difficult than in Ticonal G, since the addition of the titanium lowers the grain size. Luteijn and de Vos (1956) succeeded in preparing crystal oriented Ticonal XX by using very pure starting materials and melting them in crucibles of pure aluminium oxide in an atmosphere of pure argon, before drawing rods containing large columnar crystals. The demagnetization and energy product curves for this material are shown in fig. 7.7, and electron microscope pictures in fig. 7.2. The specific results are given as: composition, 15% Ni, 7% Al, 34% Co, 4% Cu, 5% Ti;  $H_c = 1315$  oersted,  $B_r = 1.18 \times 10^4$  gauss,  $(BH)_{\max} = 11.0 \times 10^6$  gauss-oersted. The last quantity is understood to have reached  $12.0 \times 10^6$  gauss-oersted in later developments.

These spectacular advances were accompanied by further structural investigations. Koch *et al.* (1957, see also v.d. Steeg and de Vos 1956) investigated a variety of Alnico-type materials with additions. The phase relationships revealed several interesting results. For Ticonal G an ordered



b.c.c. phase, equivalent to  $\alpha_2$  of fig. 7.1, is alone present above 1200°C. Between this temperature and 850°C this phase is in equilibrium with a f.c.c. phase which is, however, metastable and transforms to a b.c.c. structure on quenching; it is then observable as finely divided, needle shaped precipitates in the b.c.c. matrix. Between 850° and 900°C the precipitation is very slow and first takes place at grain boundaries. Below 850°C a disordered b.c.c. phase precipitates, although the appearance of the x-ray lines points, as in earlier work, to this process being incomplete. This phase is equivalent to  $\alpha$  of fig. 7.1, and is believed to be Fe-Co rich. Finally, at 600°C a second f.c.c. phase appears after prolonged annealing. This phase is stable to cooling, but disappears on heating at a higher temperature.

Fig. 7.7.



Demagnetization and energy product of Ticonal XX.

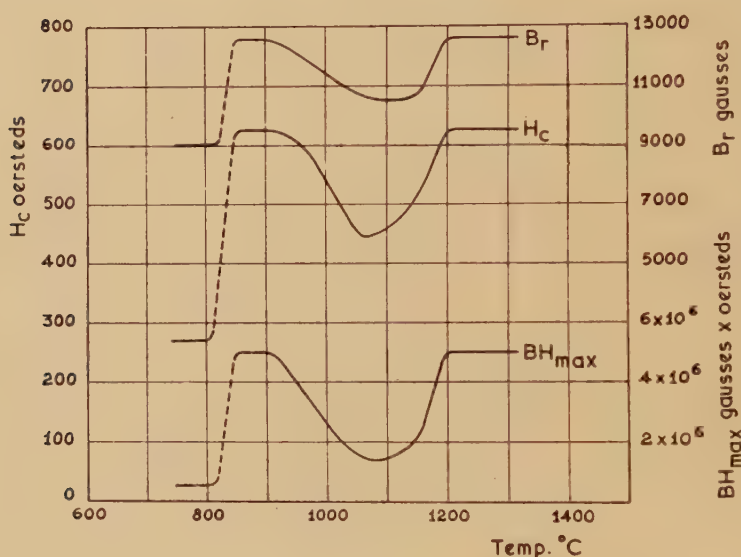
After Luteijn and de Vos (1956).

An alloy with 5% Ti, the prototype of Ticonal X, was also investigated. The same phases as in Ticonal G were found to be present. However, the high temperature f.c.c. phase can here exist over a wider temperature range, although it also transforms to b.c.c. on quenching. The low temperature f.c.c. phase is here also more easily formed. An alloy with 2% Nb was also investigated. Here an hexagonal phase ( $c=7.80$  A.U.,  $a=4.77$  A.U.), probably  $\text{Fe}_2\text{Nb}$ , was detected below 1200°C and suspected to be stable down to about 600°C in the company of the cubic phases.

The magnetic properties of Ticonal G were related by these authors to their structural results. Figure 7.8 shows how the properties depend on the temperature from which the permanent magnet treatment is started. There are two optimum ranges, viz. above 1200°C and between 850° and 900°C, in both of which a single phase condition persists prior to the formation of the high temperature f.c.c. phase. This is more easily formed between 900° and 1200°C, as shown in the phase investigations, and then

causes a deterioration of the magnetic properties, shown in fig. 7.8. It was also found that if a fully treated specimen was annealed in the range  $600^{\circ}$  to  $850^{\circ}\text{C}$ , the coercive force drops to low values, but that a re-tempering at the normal  $585^{\circ}\text{C}$  fully restores the previous properties as long as the annealing had taken place below  $650^{\circ}\text{C}$ . The experiment shows that the normal tempering process is completely reversible and that the low temperature f.c.c. phase, which forms and re-dissolves during this cyclic heat treatment, is an important factor in determining the coercive force. This phase is more easily formed in the Ti and Nb containing alloys, whose higher coercive force was interpreted on this basis.

Fig. 7.8



Heat treatment of Ticonal G.  $H_c$ ,  $B_r$ ,  $(BH)_{max}$ , magnetic properties as a function of temperature at which magnetic annealing is started, and which is followed by tempering at  $585^{\circ}\text{C}$ . After Koch *et al.* (1957).

Other results obtained in this work are concerned with quenched specimens whose coercivity is low at room temperature if quenching was started after interrupting the normal cooling process above  $750^{\circ}\text{C}$ . If, however cooling is allowed to proceed to  $600^{\circ}\text{C}$  before interruption, then quenching only reduces the coercivity to about two-thirds of normal values, since at this low temperature some tempering has already taken place. Optimum separation of the phases thus does not occur until temperatures below  $750^{\circ}\text{C}$  are reached. (The properties of the quenched magnetically soft specimens have some interest *per se*, as shown by McCaig 1957.)

The results of this investigation were summarized as follows: During the first stage of the magnetic heat treatment high coercivity is developed at high temperatures only, due to incipient precipitation of the Fe-Co rich b.c.c. disordered phase below 850°C. If this alloy is cooled to room temperature the coercivity drops, perhaps as a result of the phase segregation becoming more complete, with a resulting growth of the precipitate particles. Tempering below 750°C and preferably below 600°C causes the coercivity to have high values even at room temperature. The low temperature f.c.c. phase which is here formed may cause differences in magnetization in the b.c.c. two-phase structure. These conclusions are amenable to fuller investigation of the magnetic properties of these alloys at various stages of the heat treatment.

### 7.7. Related Investigations

In the previous sections a discussion is given of the experimental evidence regarding the structure of these complex alloys, based on metallurgical, domain pattern, magnetostriction and torque measurements. Valuable additional evidence may also be obtained from other related investigations.

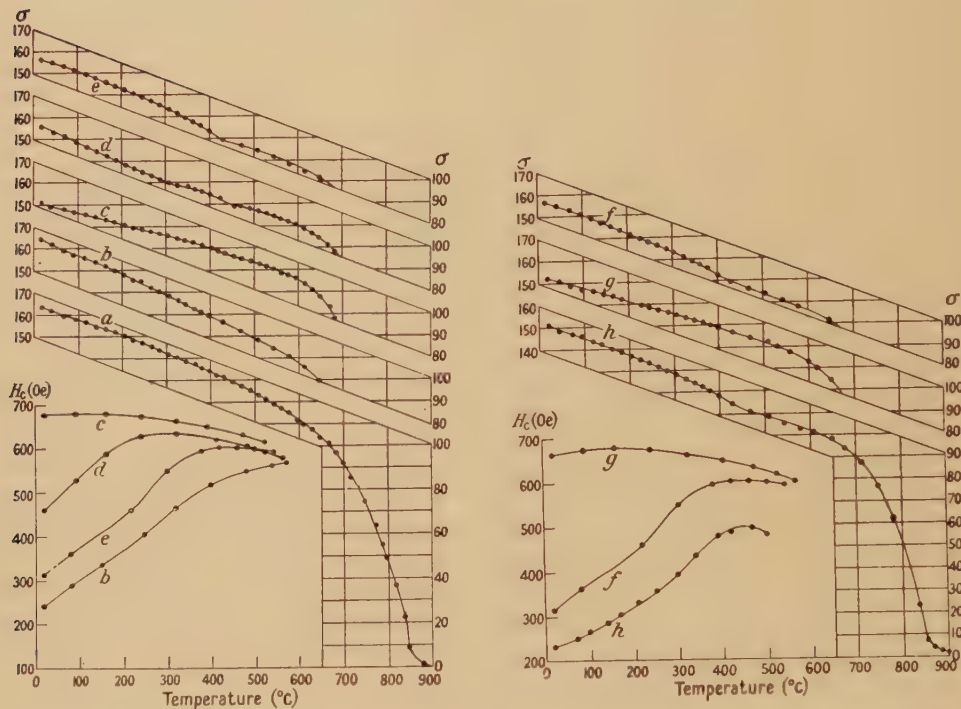
Although Snoek (1939) was able to draw significant conclusions about the structure of these alloys from a knowledge of the internal demagnetizing factor  $N_i$ , obtained from the slope of the anhysteretic magnetization curve, this method has only rarely been used since then. Néel *et al.* (1943) measured  $N_i$  for a Mishima alloy, and Bulgakov (1950) for the anisotropic alloy Magnico. Gould and McCaig (1954) then investigated Alcomax III and found that for this material  $N_i$  is also anisotropic, having values 0.01 and 0.5 in the preferred and perpendicular directions respectively. These results imply an anisotropic distribution of the 'air gaps' (more weakly magnetic phase), in general agreement with the structural evidence. It would be interesting to extend such measurements to materials prepared by the different types of heat treatment referred to earlier.

The measurements of Sucksmith (1939), who found magnetic analysis, i.e. measurements of magnetization, temperature curves, useful for studying phase relationships, have also been extended to anisotropic materials. Pawlek and Reichel (1955) investigated in this way the material Alnico 400. A specimen, field cooled from 1250°C, was heated to above the Curie point and then cooled down again. A slight kink (indicative of two phases with different Curie points) was observed at 400°C on heating, and also during cooling, although the remanence and coercivity had by then dropped to low values. The coercivity, temperature curve for this specimen showed an initial increase with a maximum at 600°C; such behaviour had been observed earlier by Jellinghaus (1943) and Bulgakov (1949). For a fully tempered specimen Pawlek and Reichel observed no kink in the magnetization, temperature curve, and here the coercivity, temperature curve shows a steady decrease. On cooling this optimum specimen from above the Curie point, there is again evidence of a second phase.



This type of investigation has been considerably extended by Clegg and McCaig (1957); they investigated Alcomax III after various heat treatments and measured the temperature variation of both magnetization and coercive force. The results are shown in fig. 7.9; here curve *c* corresponds to the normal optimum heat treatment for Alcomax, involving a double tempering. The results are difficult to interpret in full detail; kinks in the magnetization curves indicate the presence of two well defined phases with different Curie points, and these correspond to coercivities which are

Fig. 7.9



Saturation magnetization and coercivity, temperature curves of Alcomax III, (a), quenched 1250°C; (b), field cooled 1250°C 1.2 deg sec<sup>-1</sup>; (c), (b) + tempered 48 hours 590°C + tempered 48 hours 560°C; (d), (b) + tempered 48 hours 650°C; (e), (b) + tempered 4 hours 700°C; (f), same as (e); (g), (f) + tempered 16 hours 590°C; (h), (g) + tempered 4 hours 700°C. After Clegg and McCaig (1957).

relatively low and exhibit temperature maxima. Below the kinks both phases are magnetic, with different coercivities, thus reducing the bulk coercivity of the material below that of the phase with the higher Curie point. Above the kinks there is only one phase with a normal and normally varying relatively high coercivity. For the optimum specimens (c), (g) the magnetization and coercivity curves are both normal. Here, then, the two phases are present in an incompletely segregated state with a continuous

range of Curie points, a result in agreement with the structural investigations described earlier. The cyclic heat treatment of Koch *et al.* (1957), discussed above, was also applied in the present investigation. The results are shown in fig. 7.9, curves (f), (g), (h), this constituting a cycle during which the permanent magnet properties are first improved and then spoilt again.

Tenzer and Kronenberg (1958), in a magnetic analysis of fully treated Alnico V, observed a kink in the magnetization curve at between 700° and 730°C, indicating the presence of two distinct phases in the optimum state. An analysis of magnetization curves for a range of mixtures of two phases enabled them to determine their compositions in Alnico V as Fe-Ni-Al weakly magnetic matrix, 22% by volume, and Fe<sub>2</sub>Co precipitates, in reasonable agreement with other results.

The variation near room temperature of the remanence and coercivity is of great practical importance in the application of permanent magnets, but in general little fundamental information is obtainable from such data. A general review of permanent magnet stability is given by Gould (1958). Tenzer (1957) was able to relate the remanence change to the phase relationships. Clegg (1955) and Clegg and McCaig (1958) investigated the low and high temperature stability of Alnico-type magnets, and Roberts (1958) described similar measurements up to 600°C. Bulgakov (1949) investigated the temperature variation of coercivity of some alloys between -200° and +400°C, and observed a positive temperature coefficient for untempered Magnico, in agreement with the results discussed above. Lockhorst *et al.* (1954) observed the coercivity of two Ticonal specimens to have marked minima near 60°K. The increase at low temperatures may be due to the stabilization of very small precipitate particles which are superparamagnetic at room temperature. In a different type of thermal investigation Bates and Simpson (1955) measured the heat changes over the hysteresis cycle of some permanent magnet alloys.

Finally reference should be made to the measurements of the magnetic viscosity in these alloys (Bulgakov and Kondorsky 1949, Street and Woolley 1949, 1950, 1956, Street *et al.* 1952 a, b, Phillips *et al.* 1954, Barbier 1954, Yamada 1955, Kussmann and Yamada 1956, and others). The results are difficult to relate directly to those of the other investigations; they are generally interpreted in terms of wall motions, but partial thermal instabilities in small precipitate particles would also lead to viscosity effects.

## § 8. OTHER PERMANENT MAGNET ALLOYS

Apart from the complex alloys discussed in § 7, there are very many other permanent magnet alloys of considerable scientific and technological interest. None of these have been as useful as the Alnico-type materials, either due to inferior permanent magnet performance or to the expense of the component metals (e.g. platinum). The discussion in this section is confined to those materials which have received the widest attention, and

it is not intended to be fully comprehensive. Among omissions [the Heusler alloy Silmanal will be noted; this has not been fully investigated (Geisler 1951a).

### 8.1. Cu-Fe-Ni

The phase diagram of this alloy system has been investigated by Köster and Dannöhl (1935) and Bradley, Cox and Goldschmidt (1941) and others (see Haughton and Prince 1956 for a full bibliography for this and other alloy systems). Early investigations on magnetically hard alloys in this system were due to Dahl *et al.* (1935) and Neumann (1935). Dahl *et al.* found that coercivities about 300–400 oersted could be attained for alloys with compositions close to 60% Cu, 10% Fe, 30% Ni after slow cooling from 1050°C, and slightly lower values after air quenching (which by itself produces low coercive alloys) followed by tempering for 2 hours at 700°C. The magnetically hard alloys were found to be mechanically soft, and the magnetic hardness could be improved by cold working. Neumann (1935) obtained even higher coercivities for an alloy with 68% Cu, 12% Fe, 20% Ni after oil quenching from 1000°C and tempering for 2 hours at 600°C.

Neumann *et al.* (1937) later extended the magnetic measurements, investigating a large number of ternary alloys grouped about the composition 60% Cu, 20% Fe, 20% Ni. Optimum remanence and coercivity were attained by quenching from 1000°C and tempering for a short time at 650°C. The maximum value of  $(BH)_{\max}$ ,  $0.5 \times 10^6$  gauss-oersted, was obtained at the composition 59% Cu, 18% Fe and 23% Ni, where the coercive force is 390 oersted. Neumann *et al.* also investigated the effect of severe cold working and further heat treatment. The magnetic properties were all found to be improved by this means,  $(BH)_{\max}$  values up to about  $1.5 \times 10^6$  gauss-oersted being now attainable. The cold working induced a considerable anisotropy in the magnetic properties, the remanence, coercivity and energy product all being larger in the rolling direction than perpendicular to it.

Legat (1937) and Dannöhl (1938) investigated the properties of iron-rich alloys with about 15% Cu, 15% Ni. Legat found that for this composition maximum coercivities 300 oersted were obtained by quenching from 1250°C and tempering for  $\frac{1}{2}$  hour at 600°C. Dannöhl improved the coercivity slightly but the remanence considerably for an alloy with only 8% Cu, 12% Ni; the hardening was believed to be a result of the presence of an austenitic phase and copper rich precipitates. Iron-nickel rich alloys containing only small amounts of copper are, of course, magnetically soft: Bumm and Müller (1938) found that precipitation of copper causes lattice distortion and slight magnetic hardening.

Bragg (1943) has summarized experiments on these alloys performed at Cambridge. Bradley (1940) investigated by x-rays the precipitation process in an alloy with 50% Cu, 12.5% Fe, 37.5% Ni ( $\text{Cu}_4\text{FeNi}_3$ ), heat treated so that complete phase segregation (Köster and Dannöhl 1935) did not take place. By cooling from 800°C at 10°C per hour the two phases,

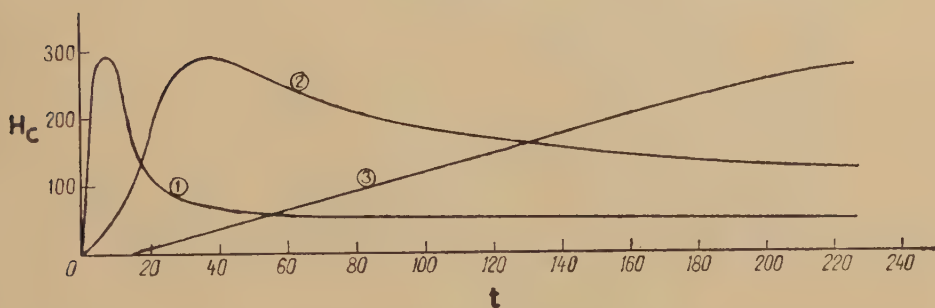


one rich in Cu, the other in Fe-Ni, were in an intermediate state of segregation and had a tetragonal crystal structure, the f.c.c.  $\gamma_1$  phase (Bradley call it  $\alpha$ ) with axial ratio slightly above 1 and  $\gamma_2(\alpha')$  slightly below 1. The coherence between these two phases and the original single phase alloy is demonstrated by the fact that the  $c$ -axis has the same length in all three cases. The two semi-coherent phases  $\gamma_1$  and  $\gamma_2$  were believed by Bradley to be present as alternating lamellae of thickness about  $0.01\mu$ . The phase diagram of the alloys in the neighbourhood of the  $\gamma_1 + \gamma_2$  field was further investigated by Bradley *et al.* (1941).

Later Daniel and Lipson (1943, 1944, see also Daniel 1948) showed that in an even earlier stage of phase segregation the original f.c.c. single phase structure is distorted by sinusoidal modulations in the lattice spacings, 'rarefactions' alternating with 'compressions'. This type of structure was manifested by the appearance of 'side bands' flanking the normal x-ray lines, and was observed for  $\text{Cu}_4\text{FeNi}_3$  quenched from  $1000^\circ\text{C}$  and then tempered for one hour at  $650^\circ\text{C}$ . By altering the time  $t$  and temperature  $T$  of this tempering treatment, it was found that the 'wavelength'  $Q$  of the sinusoidal modulations varies as

$$Q = A \ln t + \text{function of } T; \quad . . . . . (8.1)$$

Fig. 8.1

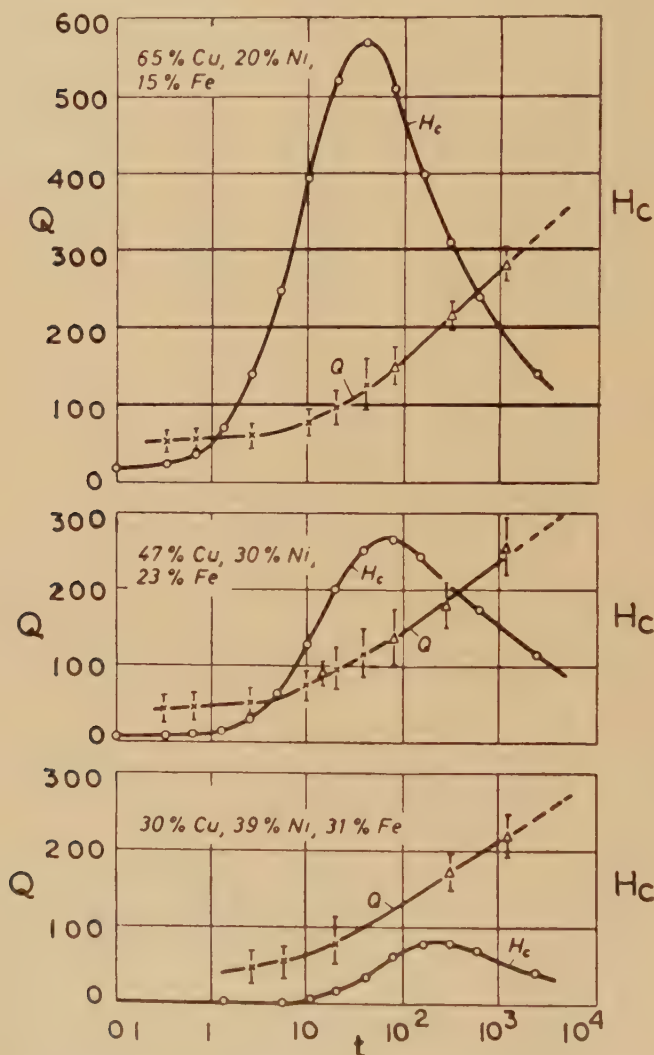


Tempering treatment of  $\text{Cu}_4\text{FeNi}_3$ .  $H_c$ , coercive force, oersted;  $t$ , time of treatment, hours, at (1)  $750^\circ\text{C}$ , (2)  $650^\circ\text{C}$ , (3)  $550^\circ\text{C}$ . From Hoselitz (1951), after Sucksmith (1945).

$Q$  was found to range from 20 to about 110 unit cell lengths. As  $t$  increased to large values, Daniel and Lipson observed the side band structure to change to Bradley's two-phase tetragonal structure, to which it bears some correspondence in that the modulations already involve periodic changes in composition. Eventually complete phase segregation into  $\gamma_1$  and  $\gamma_2$  takes place. This general picture of the hardening process was later verified by Geisler (1951 a) on the basis of x-ray and microstructure investigations. Hargreaves (1951) carried out similar measurements and amended Daniel and Lipson's interpretation of the side band phenomenon by suggesting rectangular rather than sinusoidal modulations; the problem has also been discussed by Guinier (1955).

Following Lipson's x-ray investigations, Sucksmith (1945) measured the coercive force of the alloys  $\text{Cu}_4\text{FeNi}_3$  and  $\text{Cu}_{10}\text{Fe}_3\text{Ni}_7$  (50% Cu, 15% Fe, 35% Ni), which were heat treated at 550°, 650° and 750°C for various lengths of time after quenching from 1100°C. The results are shown in fig. 8.1, which demonstrates how optimum hardness is attained at a stage of tempering where the Lipson side band structure is developed. The

Fig. 8.2



Periodicity and coercivity in Cu-Fe-Ni.  $Q$ , wavelength in units of cell lengths;  $H_c$ , coercivity, oersteds;  $t$ , ageing time, hours. Crosses, X-ray values; triangles, electron microscope values. After Biedermann and Kneller (1956).

variation of  $H_c$  with the wavelength  $Q$  was determined to establish this point; it was found that  $H_c$  did not rise to high values until  $Q$  had reached critical values about 30 unit cell lengths, depending on the tempering temperature; the maxima in fig. 8.1 correspond to  $Q$  about 150 unit cell lengths. This picture of magnetic hardening fits in well with the classical stress theory of coercivity which gives, with  $\sigma$  the stress amplitude,

$$H_c \simeq (2\delta/l)(1 + 2\delta^2/l^2)^{-1}(\lambda\sigma/I_0). \quad . \quad . \quad . \quad . \quad . \quad (8.2)$$

Here  $l$  is the wavelength of the stress variation and may be identified with  $Q$  in the present connection. A complete analysis of these and related magnetostriction data on the basis of (8.2) has not been carried out.

Table 8.1. Properties of Cu-Fe-Ni.  $Q$ , wavelength of periodic modulation in units of cell lengths;  $D$ , effective widths of ferromagnetic platelets;  $(H_c)_{\max}$ , coercive force in state of optimum hardness corresponding to  $Q$ ,  $D$  values given. After Biedermann and Kneller (1956).

Alloy no.	Cu (%)	Fe (%)	Ni (%)	$Q$	$D$ ( $\mu$ )	$(H_c)_{\max}$ (oersted)
1	65	15	20	125	0.014	570
2	47	23	30	135	0.024	266
3	30	31	39	165	0.043	81

A comprehensive investigation on magnetically hard Cu-Fe-Ni alloys was reported by Biedermann and Kneller (1956), who covered eight alloys in the ternary diagram. X-ray investigations of the specimens quenched from 1000°C and tempered for various periods of time at 600°C revealed the presence of side bands as in Lipson and Daniel's work. The wavelength  $Q$  is shown as a function of ageing time in fig. 8.2 for three of the alloys. For very long periods of ageing (over 50 days) the x-ray evidence showed that then the phase segregation had proceeded to the Bradley stage of two distinct tetragonal phases in lamellar form. The process was also followed by electron microscope observation, and rough values of  $Q$  obtained by this means are also shown in fig. 8.2 (triangles). This gives, in addition, the variation of the coercive force, which is seen to have its maximum value in a range of rapid increase of  $Q$ , but long before the appearance of well-defined lamellar precipitates. From the values of  $Q$  and the details of the ternary diagram it was, however, possible to estimate the effective thickness  $D$  of those regions in the alloy which may be regarded as approximately plate shaped and which are Fe-Ni rich and hence strongly magnetic, compared with the remainder of the alloy which is copper rich. The values of  $Q$  and  $D$  for the three alloys in their state of maximum coercive



force are given in table 8.1. These iron-nickel rich regions are regarded in Biedermann and Kneller's discussion as magnetically equivalent to ferromagnetic particles with flattened ellipsoidal shape; from estimates of the critical sizes and coercive forces of these particles the general trend of the observations for alloy No. 1 is then reasonably well interpreted in terms of shape anisotropy. For alloy No. 3 the low coercive force is regarded as evidence for domain wall motions, and for alloy No. 2, with intermediate iron and nickel content and particle size, the decrease of  $H_c$ , cf. alloy No. 1, as evidence for stronger particle interactions as well as incipient multi-domain effects. Biedermann and Kneller also measured the saturation and remanent magnetization, the magnetic viscosity constant, mechanical hardness and electrical resistance. Among many interesting data bearing on the phase segregation process it may be mentioned that an approximate proportionality was established between the coercivity and saturation magnetization of alloys with varying composition, but that no correlation exists between magnetic hardness and lattice strains and magnetostriction.

Other measurements on Cu-Fe-Ni alloys include those of Hibbard (1956), who concluded from torque curve measurements at low and high fields that, as for the Mishima alloy (Nesbitt *et al.* 1954; cf. § 7), magneto-crystalline anisotropy effects are relatively important for an alloy with 66% Cu, 17% Fe, 17% Ni. Rotational hysteresis measurements were reported by Jacobs (1957).

The alloys have been manufactured commercially under the names Cunife I (60% Cu, 20% Fe, 20% Ni) and Cunife II (50% Cu, 27.5% Fe, 20% Ni, 2.5% Co). Their mechanical softness makes it possible to manufacture them in wire form, and they are then reported to have been used for magnetic recording purposes. Cooter and Mundy (1957) have reported magnetic measurements on very thin Cunife wires (diameter down to about  $100\mu$ ). Their coercive force and maximum energy product was found to increase on cold drawing if this is followed by 1 hour's heat treatment at about  $600^\circ\text{C}$  and as long as the reduction in area is less than about 85%. The largest  $(BH)_{\text{max}}$  value observed was about  $1.2 \times 10^6$  gauss-oersted.

## 8.2. Cu-Ni-Co

Permanent magnet alloys in this system are in many respects similar to those containing iron. The first investigations were those of Volk *et al.* (1938) and Dannöhl and Neumann (1938). Optimum magnetic hardness ( $H_c$  almost 800 oersted for the alloy 50% Cu, 25% Ni, 25% Co) was attained after 1 hour's tempering at  $700^\circ\text{C}$ . In this state an incipient two-phase structure was detected from x-ray observations, phase segregation tending to take place at grain boundaries. The two phases are both f.c.c. and tend to be Ni-Co and Cu rich. The coercivity was found to depend sensitively on the composition, as well as on the tempering time and temperature. Whereas maximum coercivity demands a high copper content, the optimum value of  $(BH)_{\text{max}}$ , about  $1 \times 10^6$  gauss-oersted, is reached for a more copper deficient alloy (35% Cu),

whose remanent magnetization is higher. For these alloys, also, good mechanical properties accompany magnetic hardening.

Geisler and Newkirk (1949; cf. also Geisler 1950, 1951a, 1953) carried out an x-ray study of the hardening process in an alloy 50% Cu, 21% Ni, 29% Co, and found that the cobalt rich precipitates first form on the (100) planes of the matrix, with which they are still coherent. Both precipitates and matrix are in this state face-centred tetragonal, but the distortion is lost after further ageing. In this advanced state of phase segregation the two lattice constants differ from each other and bracket that of the original single phase material (3.53, 3.56, 3.59 Å.U.). The precipitate sizes observed in the optimum state were found to be close to critical for single domain behaviour, but Geisler ascribes the large coercive forces observed (800 oersted after 4 hours at 700°C, 900 oersted after 100 hours at 600°C) more to the coherence strains associated with the lattice tetragonality.

Biedermann and Kneller (1956) also investigated the alloy 50% Cu, 21% Ni, 29% Co. They found that the segregation process is similar to that occurring in the Cu-Fe-Ni alloys. Contrary to the findings of Geisler it was observed that the quenched alloy develops an x-ray side band structure after heating for a short time at 700°C, followed by the appearance of tetragonal lines after 80 minutes, and finally by complete segregation. The precipitation process is thus the same as that which takes place in the iron alloys. The difference between their results and those of Geisler and Newkirk (1949) is ascribed by Biedermann and Kneller to differences in the cooling speeds; Geisler's treatment led to a material for which phase segregation was already advanced, as witness its already high coercive force (100–150 oersted), compared with that attained by Kneller after rapid quenching (6 oersted).

Commercial alloys containing Cu, Ni and Co have been manufactured as Cunico I (50% Cu, 21% Ni, 29% Co) and II (35% Cu, 24% Ni, 41% Co), the last with  $(BH)_{\max} = 1 \times 10^6$  gauss-oersted. A material produced by sintering (Steinitz 1946), and known as Permet, contains 45% Cu, 25% Ni, 30% Co and has a high coercivity 800 oersted.

### 8.3. Fe-Co-W

The first investigations of the phase diagram of this system were carried out by Köster and Tonn (1932a), and the permanent magnet properties were described by Köster (1932). After quenching an alloy with 67% Fe, 15% Co, 18% W from 1300°C and tempering at 700°C to produce a heterogeneous dispersion hardened alloy, he attained a coercivity 150 oersted and high remanence  $1.15 \times 10^4$  gauss. Similar coercivity results were obtained by Seljesater and Rogers (1932) for an alloy 48% Fe, 24% Co, 28% W, but here the remanence is lower. In both investigations mechanical hardness was found to reach maximum values for a tempering temperature some 100°C below that for optimum magnetic hardness.

Rogers (1933) extended these investigations to other compositions, and obtained  $H_c = 250$  oersted after tempering at 700°C for an alloy with 20% Fe,

50% Co, 30% W. The remanence was, however, low, and these alloys have not been manufactured commercially.

#### 8.4. Fe-Co-Mo, Fe-Mo-W, Fe-Mo

Fe-Co-Mo alloys, relatively rich in iron, were also investigated by Seljesater and Rogers (1932), Köster and Tonn (1932 b) and Köster (1932). In the last work a dispersion hardened alloy with 70% Fe, 12% Co, 18% Mo had a maximum coercivity 350 oersted, and this alloy had a remanence  $7.3 \times 10^3$  gauss. For a range of compositions the remanence was found to decrease approximately linearly as the coercive force increases, as expected on general grounds.

Snoek (1938) carried out an extensive investigation on the two alloys 68% Fe, 15% Co, 17% Mo and 70% Fe, 12% Co, 18% Mo. He found that the internal demagnetizing factor reached a maximum at a tempering temperature 700°C, and that the coercivity maxima (250 and 300 oersted respectively) occur at the exactly the same point. As expected for this type of dispersion hardened alloy, maximum coercivity and heterogeneity thus occur together.

Commercial alloys in this system, known as Comalloy, Remalloy, Indalloy, contain 71% Fe, 12% Co, 17% Mo and have a maximum energy product  $1.1 \times 10^6$  gauss-oersted after quenching from 1200°C and tempering for  $1\frac{1}{2}$  hours at 685°C. For an alloy 73% Fe, 5% Co, 5% Cr, 17% Mo, Nesbitt (see Bozorth 1951 b, p. 419) attained  $(BH)_{\max} = 1.2 \times 10^6$  gauss-oersted. Greiner and Tolman (see Bozorth 1951 b, pp. 383-84) investigated other alloys in this system, and also the effects on the magnetic properties of varying the quenching and tempering temperatures.

Fe-Mo-W alloys with more than 50% Fe have been investigated by Masumoto and Shirakawa (1956). The alloys were quenched from 1300°C and tempered for 3 hours at 650°C. The phase diagram of this system is not known at present, but the ageing process is presumably similar to that in the cobalt-containing alloys. A considerable area of the ternary diagram was covered in these investigations, and fig. 8.3 shows the remanent induction, coercivity and maximum energy product. Two regions of optimum properties are close to 30% Mo, 0% W and 15% Mo, 15% W.

Figure 8.3 shows that a binary alloy with 70% Fe, 30% Mo has a coercive force 425 oersted. Alloys in this system have been known for many years to have a high coercivity. Seljesater and Rogers (1932) first reached 220 oersted for an alloy with 23% Mo. Messkin and Somin (1936) determined the saturation magnetization  $I_0$ , magnetocrystalline anisotropy constant  $K$  and coercive force of Fe-Mo alloys after heat treatment. They only obtained a coercivity 50 oersted at 20% Mo. It is of historical interest that this was compared with the anisotropy field  $K/I_0$  in an attempt to verify Akulov's theory (1933, cf. § 2); this was found to be about 500 oersted at 20% Mo, i.e. much higher than Messkin's but of the order of Masumoto's value, shown in fig. 8.3.

An extensive investigation of the magnetic properties of Fe-Mo alloys has been reported by Sucksmith and Margerison (1950). They quenched



alloys with 10, 15, 20% Mo from 1350°C, and then tempered them between 550° and 750°C for various periods of time. This treatment causes the precipitation of the  $\epsilon$ -phase, which contains  $\text{Fe}_3\text{Mo}_2$ , is non-magnetic and forms plate-like structures. The coercive force was found to increase rapidly up to about 100 oersted at 600°C and then to decrease slowly as precipitation proceeded. The results were interpreted in terms of the shape anisotropy of the strongly magnetic, iron-rich regions which the plate-like precipitates tend to isolate. The relation, between coercivity and saturation magnetization was found to be linear, which supports this interpretation. From the slopes of the  $H_c$ ,  $I_0$  curves it was possible to estimate the effective shape anisotropy coefficient, and this was found to be small. Some account was also taken of the strong interactions between the iron-rich regions (Wohlfarth 1948, unpublished), but only qualitative agreement could be obtained with the observations, for example, between calculated and observed curves relating  $H_c$  with the initial permeability. Sucksmith also achieved a certain amount of effective 'particle' alignment by precipitating the  $\epsilon$ -phase in a magnetic field  $3 \times 10^3$  oersted at 700°C; the reduced remanence observed was 0.78.

#### 8.5. Fe-Co-V

These alloys were first investigated by Köster and Lang (1938) and later developed as permanent magnet materials by Nesbitt and Kelsall (1940). They prepared alloys with compositions in the range 30–52% Fe, 36–62% Co, 6–16% V with coercive forces up to about 400 oersted and  $(BH)_{\max}$  up to about  $2.8 \times 10^6$  gauss-oersted. The alloys were found capable of being rolled and machined, and were used for magnetic recording purposes when in tape or wire form. As reported briefly in 1940, the final heat-treatment was preceeded by severe cold working. Fuller details were given later by Nesbitt (1946). He prepared an alloy (Vicalloy I) with 38% Fe, 52% Co, 10% V, for which ageing at 600°C may be preceeded either by slow cooling or by quenching from temperatures in the wide range 800° to 1300°C, but which were not cold worked. This alloy had coercivity 300 oersted and  $(BH)_{\max} = 1 \times 10^6$  gauss-oersted. The cold worked alloys (Vicalloy II, containing 35% Fe, 52% Co, 13% V) were prepared by wire drawing up to a reduction in area 98%. The maximum energy product could be improved up to  $3.5 \times 10^6$  gauss-oersted if this process is followed by a tempering treatment of 8 hours at 600°C. The energy product was found to increase with the V content (up to 14%) and the degree of cold working. These alloys were found to be anisotropic, with improved magnetic properties along the direction of elongation. Figure 8.4, curves 2 and 4, show the difference in the demagnetization and energy curves parallel and perpendicular to the drawing direction, curve 3 for the same alloy cold worked so as not to produce any appreciable anisotropy. The anisotropy is pronounced only in the remanent magnetization, the coercive force being almost completely unaffected.

By reference to the phase diagram of Köster and Lang (1938, see also Bozorth 1951 b, p. 201, where an amended diagram due to Greiner and

Fig. 8.3

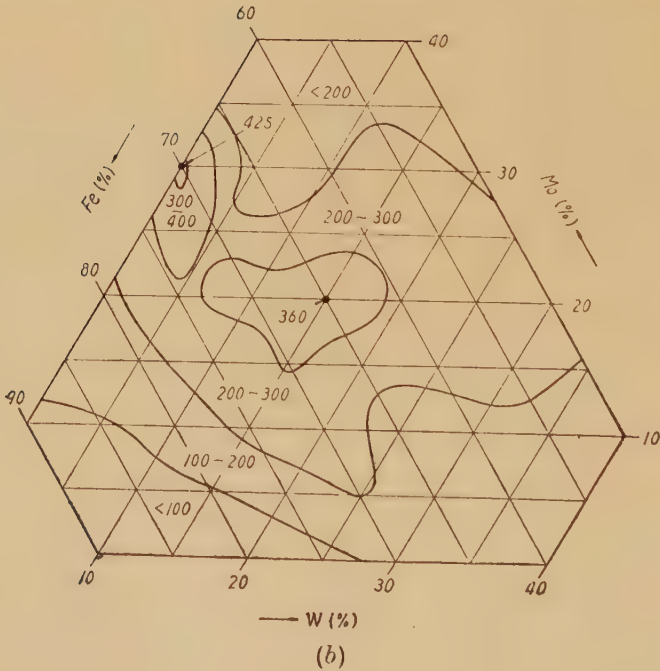
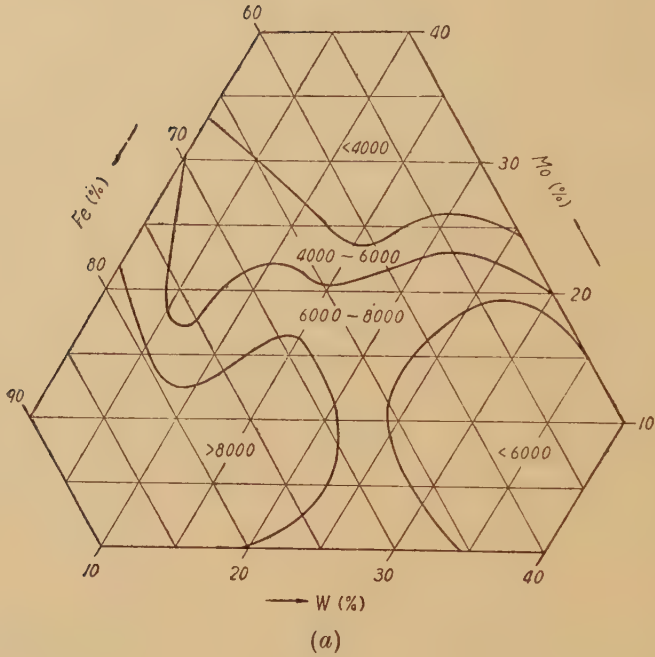
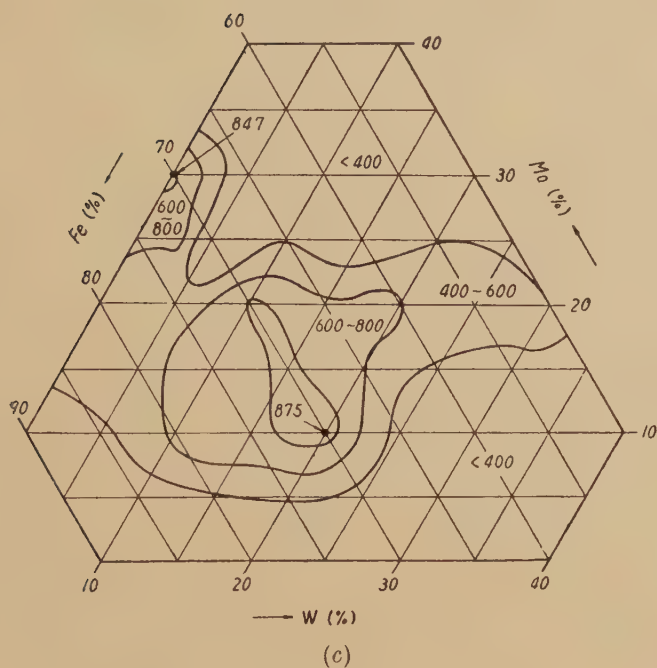
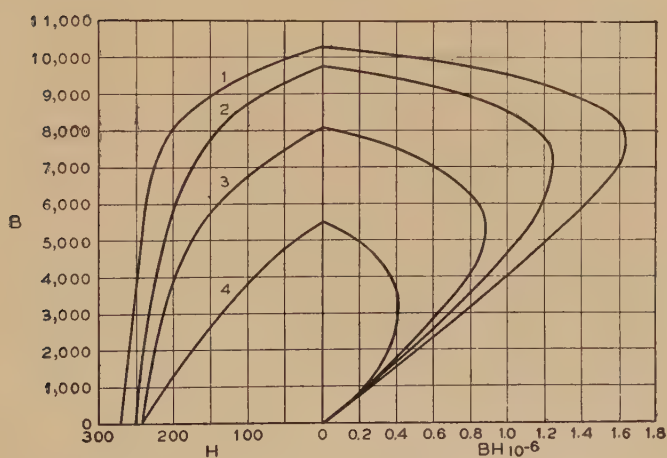


Fig. 8.3 (continued)



Magnetic properties of Fe-Mo-W. (a),  $B_r$  in gauss; (b),  $H_c$  in oersted; (c),  $(BH)_{\max} \times 10^{-3}$  in gauss-oersted. After Masumoto and Shirakawa (1956).

Fig. 8.4



Anisotropy in Vicalloy II. After Nesbitt (1946).



Ellis is given) the magnetic hardening of these alloys was understood in terms of the precipitation of a f.c.c. phase in the b.c.c. matrix during the ageing treatment at 600°C. The cold working then apparently acts to align the precipitates.

Martin and Geisler (1952 a) carried out a more complete investigation of Fe-Co-V alloys in order to determine if precipitation of the f.c.c. phase, which is non-magnetic, is the complete explanation of the magnetic hardening. It was concluded from x-ray observations that the b.c.c. phase may occur either in an ordered or disordered state, and that these two phases may, under certain circumstances, coexist with each other as well as with the f.c.c. phase. Further magnetic and structural investigations then showed that the magnetic hardening could well be a result of the presence in dispersed form of the ordered b.c.c. phase rather than being due to precipitation of the f.c.c. phase. The effect of the vanadium on the hardening process is then not clear, since order-disorder changes also occur in pure equiatomic Fe-Co alloys (Ellis and Greiner 1941), and these are not magnetically hard in the massive state. Fountain and Libsch (1953) carried out structural and magnetic investigations on Vicalloy I, and concluded that the magnetic hardening is due primarily to the precipitation of the f.c.c. phase and the resulting coherency strains. The ordering reaction in the b.c.c. phase described by Martin and Geisler (1952 a) is thought to have an important influence only if ageing takes place above about 600°C where the f.c.c. precipitates tend to grow and so to relieve the strains.

The phase diagram of Fe-Co-V was later investigated again by Köster and Schmid (1955). Hibbard (1956) reported textural investigations, and these were continued by Houdremont *et al.* (1957, cf. also Fahlenbrach 1956). Extensive investigations on the effects of stresses on the magnetic properties of Vicalloy have been reported by Shur, Lushinskaya and Shubina (1957 a, b) and Lushinskaya and Shur (1957). They found that, for magnetically hard wire specimens produced by ageing at between 500° and 600°C, longitudinal elastic stresses  $\sigma$  increase both the coercivity and remanence, but that torsional stresses, while also raising  $H_c$ , decrease  $B_r$ . Optimum values were obtained for an alloy in the form of a 0.1 mm diameter wire, tempered at 500°C and loaded to 300 kg mm<sup>-2</sup>; for this  $H_c = 850$  oersted,  $B_r = 1.3 \times 10^4$  gauss, reduced remanence about 0.9 parallel to the wire, and  $(BH)_{\max} = 7 \times 10^6$  gauss-oersted. This result is ascribed to strain anisotropy effects in small particles of precipitate; the calculated value of  $dH_c/d\sigma \simeq \lambda/I_0$ , about  $10^{-9}$  to  $10^{-8}$  oersted dyne<sup>-1</sup> cm<sup>2</sup>, is in good agreement with observation. After removal of the elastic stresses, the wires return to their original properties. In order to produce materials with permanent improvement Shur prepared Vicalloy wires by means of the so-called thermomechanical treatment. This consists in applying longitudinal tensile stresses of the order 40 kg mm<sup>-2</sup> during the final tempering treatment at about 600°C. By this means the coercivity may be increased by up to 25% and the maximum energy product 40–50%. Optimum results quoted are  $H_c = 570$  oersted,  $B_r = 1.04 \times 10^4$  gauss,

$(BH)_{\max} = 4.2 \times 10^6$  gauss-oersted. The effect is believed to be due to a combination of changes in the strain anisotropy of precipitate particles and of stress induced transformations of the b.c.c. to the f.c.c. phase.

This process may have wider uses.

### 8.6. Fe-Pt

Magnetically hard iron-platinum alloys were first investigated by Graf and Kussmann (1935). A high coercive force 1800 oersted was attained for the equiatomic alloy by quenching it from the single-phase state at  $1200^\circ\text{C}$ . With a low remanence, the maximum energy product was only about  $3 \times 10^6$  gauss-oersted (cf. Neumann 1937). Structural investigations were also reported, but the result that magnetic hardening is due to the presence of a disordered b.c.c. phase in a f.c.c. matrix must now be regarded as incorrect. Later Lipson *et al.* (1941) applied a different heat treatment to the equiatomic alloy, heating for a short time at  $1500^\circ\text{C}$ , followed by air cooling, and this led to coercive forces less than 1200 oersted. The alloys were found to have an ordered f.c.t. structure with  $c/a = 0.968$ . On the basis of structural investigations, the high coercivity was ascribed to strain twinning, occurring as a result of the transformation from the high temperature cubic to the tetragonal phase. This work extended earlier investigations of Jellinghaus (1936 b), who detected an ordered tetragonal phase in the equiatomic alloy heat treated to have a coercivity 1400 oersted.

Kussmann and v. Rittberg (1950 a) observed that for the non-stoichiometric alloy with only 40 at. % Pt the saturation and remanent magnetization is much higher than for the equiatomic alloy, while the coercive force changes only slightly. For this alloy the coercive force (intrinsic) was 1900 oersted, the remanent induction  $6 \times 10^3$  gauss and  $(BH)_{\max} 3.3 \times 10^6$  gauss-oersted. The ratio of the remanent to the saturation magnetization (measured at  $2 \times 10^4$  oersted) was relatively high for the apparently isotropic alloy, namely 0.64. This result would imply that, if the magnetic hardness is due to precipitate particle effects, the anisotropy is due, at least in part, to magnetocrystalline effects which could have their origin in the tetragonal crystal structure. The interpretation of the magnetic hardness in terms of strain effects is made less attractive by Kussmann's findings that the saturation magnetostriction coefficient of the equiatomic alloy is very low, about  $1-2 \times 10^6$  compared with the values up to  $180 \times 10^6$  at lower platinum contents.

The phase diagram of the Fe-Pt system has also been re-investigated by Kussmann and v. Rittberg (1950 b). They found, in agreement with Lipson *et al.* (1941), that the FePt phase is f.c.t. with  $c/a = 0.973$ . This ordered phase can coexist with the disordered  $\gamma$  phase, analogously to the equiatomic Co-Pt alloy (see below). In view of the low magnetostriction, the magnetic hardness could thus indeed be ascribed to particle size effects of the ordered phase embedded in the disordered matrix. However, as Kussmann also found, both phases are ferromagnetic, so that the interpretation of magnetic hardness is certainly more complicated. The

magnetic hardness of powders of the fully ordered FePt phase is much more pronounced than that of the two-phase bulk material (see § 3; Weil 1948 c, 1949 c), viz.  $H_c$  values up to  $2 \times 10^4$  oersted, over 10 times the observed value for this alloy. This result implies that the hardness of the disordered  $\gamma$  phase in FePt alloy is low, thus reducing the bulk coercive force. Alternatively, the ordered tetragonal precipitates may be larger in the bulk material than are Weil's powders. Much further work on this fascinating material is evidently necessary.

### 8.7. Co-Pt

Jellinghaus (1936 b) also investigated the properties of cobalt-platinum alloys, and found that for the equiatomic alloy in the as-cast state a high coercivity (1600 oersted) was already attained. This figure could be increased to  $4 \times 10^3$  oersted after a tempering treatment of 3 hours at 650°C. Neumann (1937) quoted  $(BH)_{\max}$  almost  $4 \times 10^6$  for this alloy. Gebhardt and Köster (1940) found that, as in the iron alloys, a f.c.t. phase is formed near the equiatomic composition. Tetragonality was found to set in at about 825°C and ordering at about 520°C, the cubic and tetragonal phases being capable of coexistence. An optimum coercivity  $3.75 \times 10^3$  oersted was quoted.

In a brief account Bragg (1943) reported improvements in the permanent magnet properties of the equiatomic alloy after quenching from 1000°C and tempering for 13 hours at 600°C. The remanent induction was found to be  $5 \times 10^3$  gauss, the intrinsic coercive force  $7 \times 10^3$  oersted, but  ${}_B H_c$  only about half this value. It is not clear what significance can be attached to the quoted value of  $(BH)_{\max}$ ,  $14 \times 10^6$  gauss-oersted.

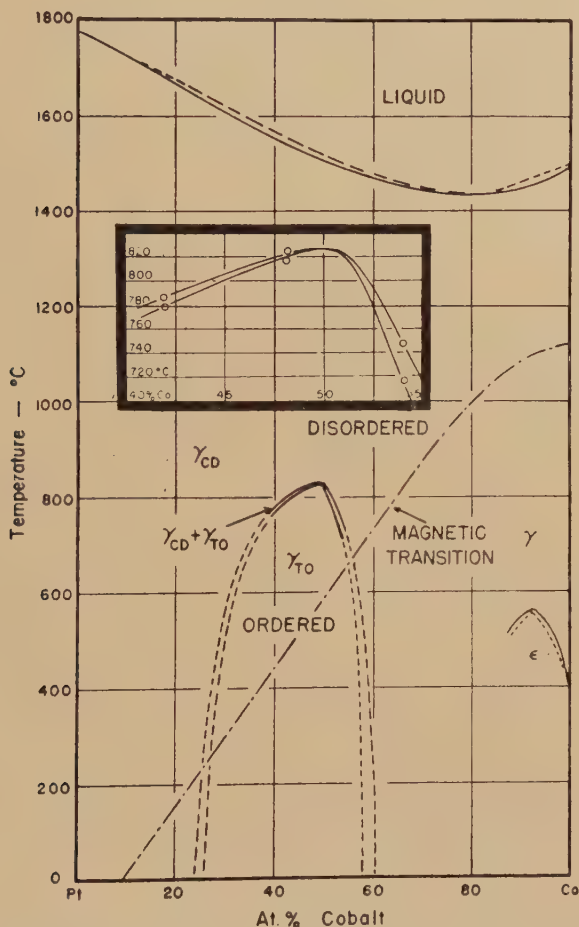
The most extensive investigation of Co-Pt alloys near the equiatomic composition has been carried out by Geisler, Smoluchowski and associates. Newkirk *et al.* (1951) revised Gebhardt and Köster's (1940) phase diagram on the basis of x-ray diffraction, microscopic and electrical resistance measurements; the new diagram is shown in fig. 8.5. Here  $\gamma_{CD}$  and  $\gamma_{TO}$  denote respectively the f.c.c. disordered and f.c.t. ordered phases. At compositions different from ideal CoPt, the  $\gamma_{TO}$  phase can coexist with  $\gamma_{CD}$  in equilibrium at high temperatures;  $\gamma_{TO}$  here appears as plate-like particles parallel to the (110) planes of the  $\gamma_{CD}$  matrix. Figure 8.5 differs from Köster's diagram in not including a field representing a disordered tetragonal phase, and from Jellinghaus, (1936 b) and Hultgren and Jaffee's (1941) in not showing a low temperature b.c.c. phase. Newkirk *et al.* (1950) reported measurements of the magnetic properties of Co-Pt alloys with 42, 48 and 54% Co (atomic), developed during the ordering reaction at 500°, 600° and 700°C. The results are shown in fig. 8.6; the magnetic hardening is attributed to strains resulting from the formation of the  $\gamma_{TO}$  platelets in dispersed form, and the subsequent softening to strain relief resulting from thermal recovery, self-deformation or recrystallization. As elsewhere, magnetic hardness may, however, also result from the properties of the platelets themselves. The high coercivity of



fully ordered CoPt powder particles (cf. § 3) can hardly be explained in terms of coherency strains.

The magnetic properties of the patented Co-Pt alloys have been summarized by Martin and Geisler (1953). The highest  $(BH)_{\max}$  reported is for the 48% Co alloys which had been cooled from 1000°C at  $1.3^{\circ}\text{C sec}^{-1}$  and then aged for 5 hours at 600°C; the resulting value was  $9.0 \times 10^6$  gauss-oersted. A more extensive description of the methods of manufacture and properties has been given by Martin (1957, 1958), covering the

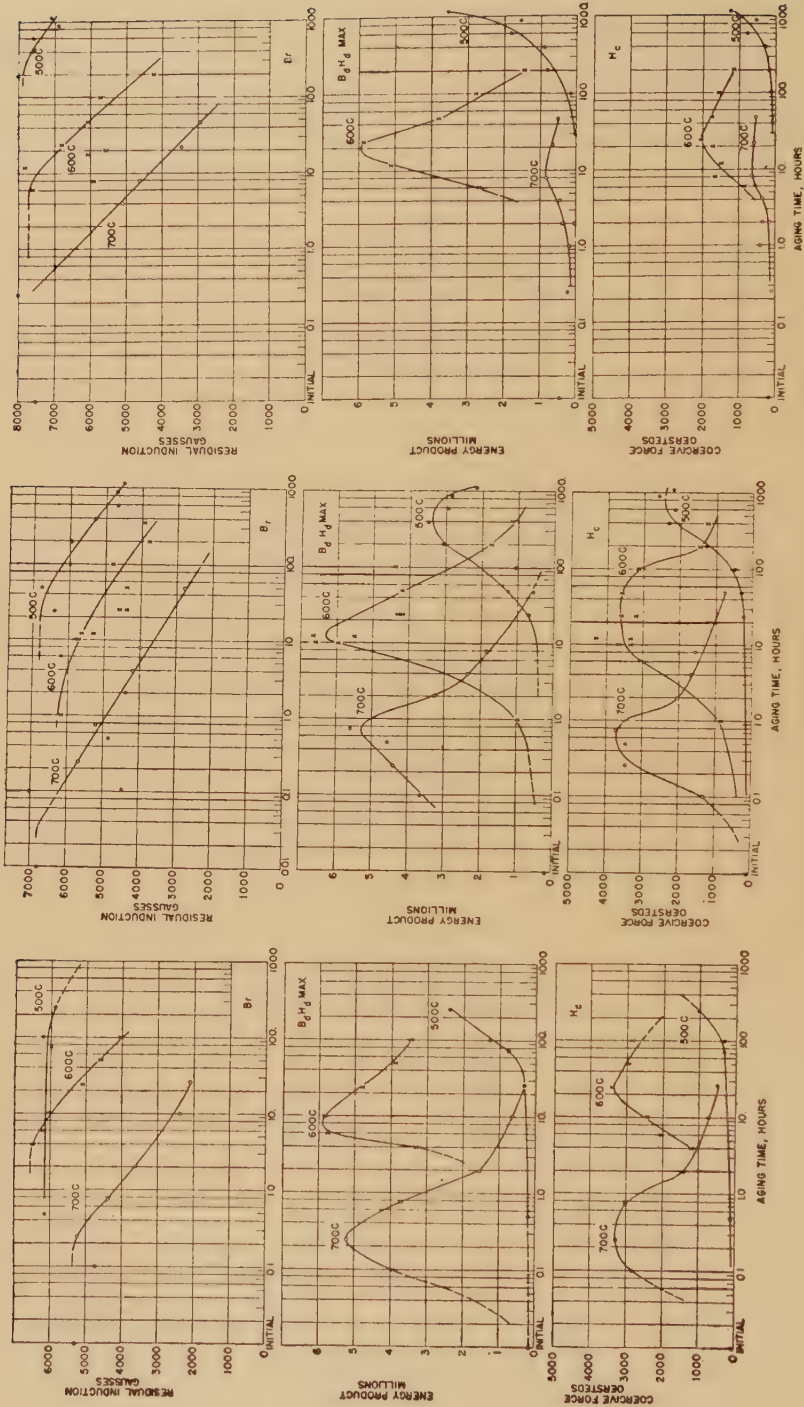
Fig. 8.5



Phase diagram of Co-Pt. After Newkirk *et al.* (1951).

range of atomic cobalt contents 30–70%. As ordering proceeds near the equiatomic composition (cf. fig. 8.5), it was observed that the saturation and remanent magnetizations decreased regularly, since the  $\gamma_{TO}$  phase has a lower magnetization than  $\gamma_{CD}$  (see also fig. 8.6). However, the coercive force and maximum energy product reach maximum values at an

Fig. 8.6



(a)

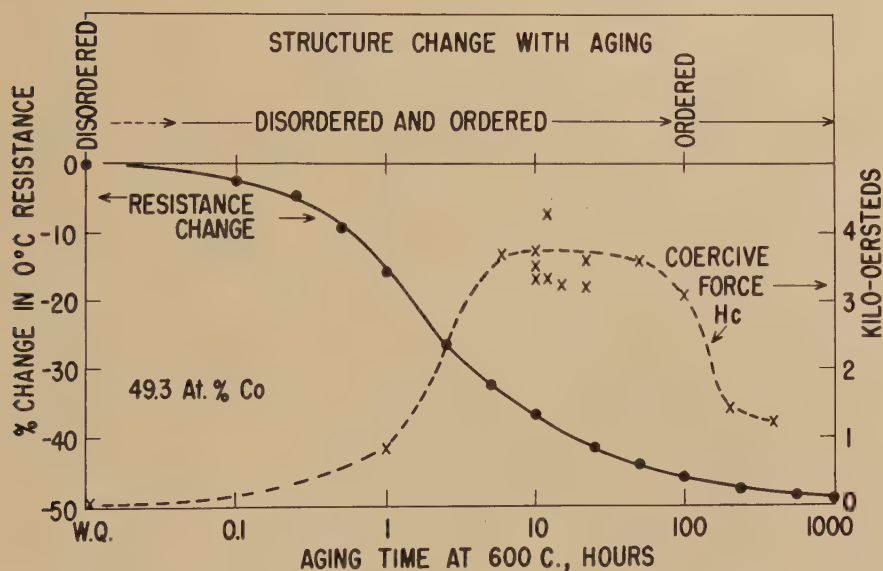
(b)

(c)

Magnetic properties of Co-Pt during ordering. (a) 42% Co, (b) 48% Co, (c) 54% Co, all atomic. After Newkirk *et al.* (1950).

intermediate state of incomplete order, as also shown in fig. 8.7; the maximum  $H_c$  corresponds to a conversion of about half the material to the ordered phase. For the 49.3% alloy, a  $(BH)_{\max} 9.0 \times 10^6$  gauss-oersted was also attained after cooling at  $1.7^\circ\text{C}$  from  $1000^\circ\text{C}$  and then ageing at  $600^\circ\text{C}$ ; for this alloy  $H_c = 4.7 \times 10^3$  oersted. The magnetocrystalline anisotropy constant of the  $\gamma_{\text{TO}}$  phase was estimated from torque curve measurements, and found to be about  $10^7 \text{ erg cm}^{-3}$ . If the magnetic hardness is thus due to the properties of the  $\gamma_{\text{TO}}$  platelets themselves, this high magnetocrystalline anisotropy would have a governing influence. It is then significant that the reduced remanence of the magnetically hardest alloys reaches high maximum values about 0.86, exactly as in the Fe-Pt alloys. Although, due to the difficulties of reaching saturation, these may be overestimates, a large reduced remanence would again be compatible with crystal anisotropy governed  $\gamma_{\text{TO}}$  particles. In the absence of other evidence, such as magnetostriction, an interpretation based on coherency strains can, however, not be ruled out, and the magnetization processes would in this case also be influenced by the large crystal anisotropy.

Fig. 8.7



Structure, electrical and magnetic properties of 49.3% Co-Pt.  
After Martin (1957, 1958).

Cobalt-platinum alloys close to the equiatomic composition are manufactured as Platinax II. This alloy is comparatively malleable and ductile before hardening, and can thus be machined, rolled or drawn, allowing complicated shapes of components to be produced. The quoted data for Platinax II are:  $B_r = 6.4 \times 10^3$  gauss, produced by a field  $2 \times 10^4$



oersted;  $H_c = 4.8 \times 10^3$  oersted;  $(BH)_{\max} = 9.2 \times 10^6$  gauss-oersted; isotropic magnetic properties. No data for the saturation induction are available, due to the immense magnetic hardness. An interesting application of this material is in the manufacture of a permanent magnet motor to drive the balance wheel of an electric watch (Anon 1957 b). Here both high  $(BH)_{\max}$  and high  $H_c$  are essential features, which are exhibited by this alloy.

*Brief notes added in proof:* After the various sections of this article were written, some further papers of relevance have appeared, which will now be briefly mentioned.

§ 2. Johnson and Brown (1959 b) calculated the coercive force of particles with mixed uniaxial and cubic anisotropies, characterizing the last by a simple 4th order term; application was intended to  $\gamma\text{Fe}_2\text{O}_3$ . Brown (1959 c) derived the frequency  $f_0$  in relation (2.5) using a method of Kramers; the calculated relaxation time agrees fairly well with Néel's (1949 b). Amar (1958 b, 1959) extended his treatment of multidomain particles by considering the motion of a single wall in an applied field; this magnetization process is relatively hard. He also suggested an interpolation formula to cover Meiklejohn's data (1953). Brown (1959 b) and Aharoni (1959) have reviewed their work on micromagnetics.

§ 3. Kronenberg (1959) carried out investigations of the fields close to small iron particles, using iron oxide colloids and electron microscope observation; he found that the particles were in the main non-uniformly magnetized. Luborsky (1958 b) extended his (1957) work on particle growth kinetics in mercury to cobalt particles, for which the process is similar to that for iron. Falk *et al.* (1959) reported on the properties of elongated iron and Fe-Co particle magnets, now in commercial production: available iron magnets have optimum  $(BH)_{\max} = 2.2 \times 10^6$  gauss-oersted and Fe-Co  $3.5 \times 10^6$  gauss-oersted. Yamartino *et al.* (1959) reported on the stability of these magnets, and Norman and Mendelsohn (1959) described the production of mouldable magnets containing iron particles coated with a thermoplastic binder. Kouvel (1959) observed exchange anisotropy effects in an Fe-Al alloy with 30% Al, FeAl type ordering and evidence for ferromagnetic and antiferromagnetic phases. These effects are also reported for many other materials, but a precise interpretation is still lacking. Goldman and Post (1959) prepared MnBi particles by reacting manganese and bismuth in mercury, vacuum distilling the mercury at low temperatures and finally annealing the powder at 400°C. Shtoltz *et al.* (1958) reported measurements of the angular variation of the coercive force of partially aligned MnBi powders of size, 9, 30, 90  $\mu$ , as well as of relatively large cobalt,  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{Fe}_2\text{O}_3$  powders; maxima in the curves were observed for the larger particles. A theoretical curve for the angular variation of multidomain particles shows an increase of  $H_c$  with angle, as expected on general grounds. Only a few of the many investigations from Shur's group could be reported in this article: much of the most

recent work is described in the issue (No. 10) of *Izvestiya* containing the above paper, and also by Shur (1959).

§ 4. Ferguson and Hass (1958) investigated the magnetic structure and vacancy distribution of  $\gamma\text{Fe}_2\text{O}_3$  by neutron diffraction. Williams *et al.* (1958) observed magnetic domains in thin transparent crystals of  $\alpha\text{Fe}_2\text{O}_3$  by using the Faraday effect; they found that the domain structure changes by applying a low field. They believe that the domain structure of haematite is a bulk property of the crystal; the results are compatible with those of Blackman *et al.* (1957).

§ 5. Schuele (1959) gave fuller details about the preparation of ferrite powders from the bi-metal oxalates. Henry (1958) obtained for the saturation magnetization of barium ferrite  $p_B = 1.64$  per iron atom, the field required for saturation being above  $3 \times 10^4$  oersted. Giron and Pauthenet (1959) fitted the high field magnetization of powdered barium ferrite to theoretical curves based on pure rotational processes (see fig. 5.2), and thus estimated  $K$  and  $I_0$ . Guillaud and Vautier (1957) gave results on the temperature and size dependence of the coercivity of barium ferrite. Sherwood, Remeika and Williams (1959) reported domain observations, using Bitter patterns and the Faraday effect, on  $\text{PbFe}_{12-x}\text{Al}_x\text{O}_{19}$ , with  $x$  up to 5.9. Curzon (1959) used the electron beam technique for domain observation of a barium ferrite crystal.

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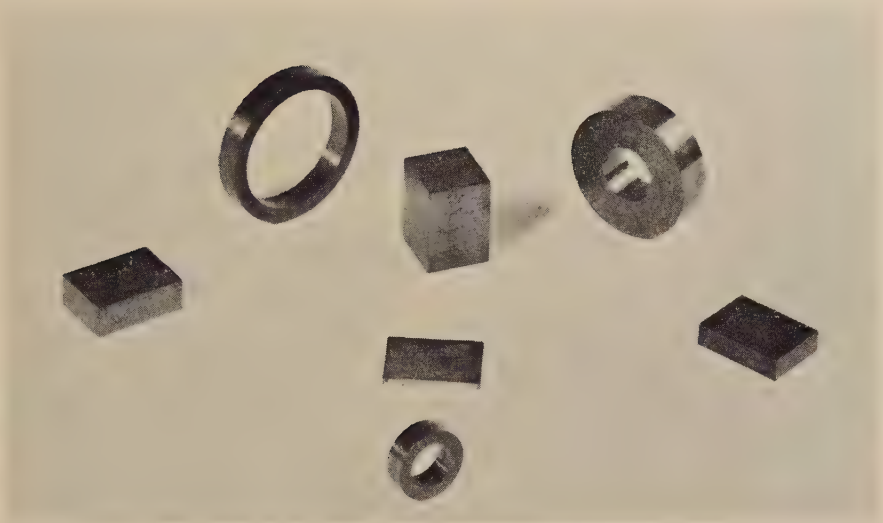
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Fig. 3.5



Elongated single domain powder magnets. Reproduced by kind permission of T. O. Paine, General Electric Company.

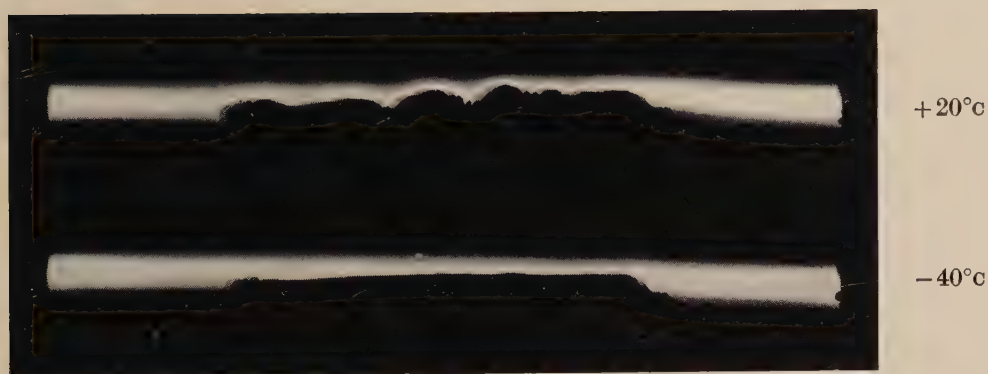
Fig. 3.6



Elongated iron particles ( $\times 100\,000$ ). From Paine *et al.* (1955 b).



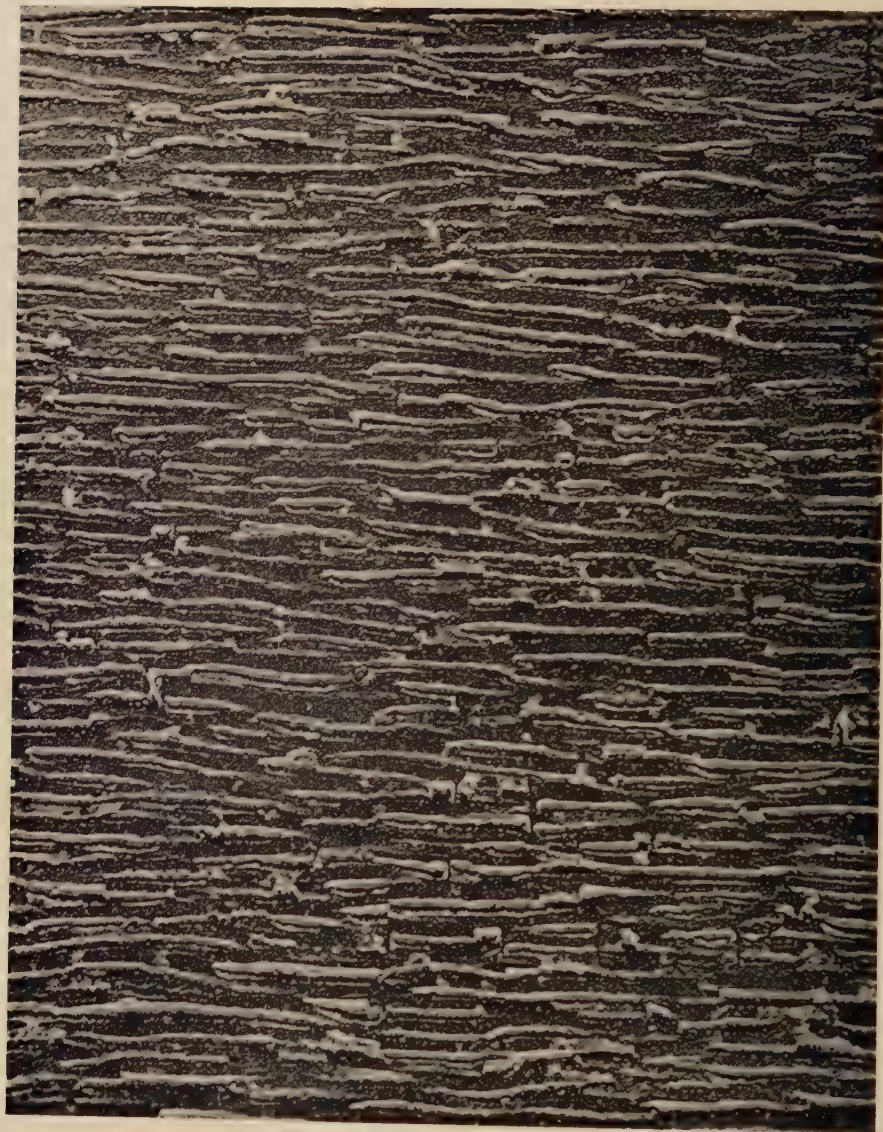
Fig. 4.8



Morin temperature  $-17^{\circ}\text{C}$

Shadow patterns of haematite crystal. Reproduced by kind permission of M. Blackman.

Fig. 7.2



(a)



Fig. 7.2 (*continued*)

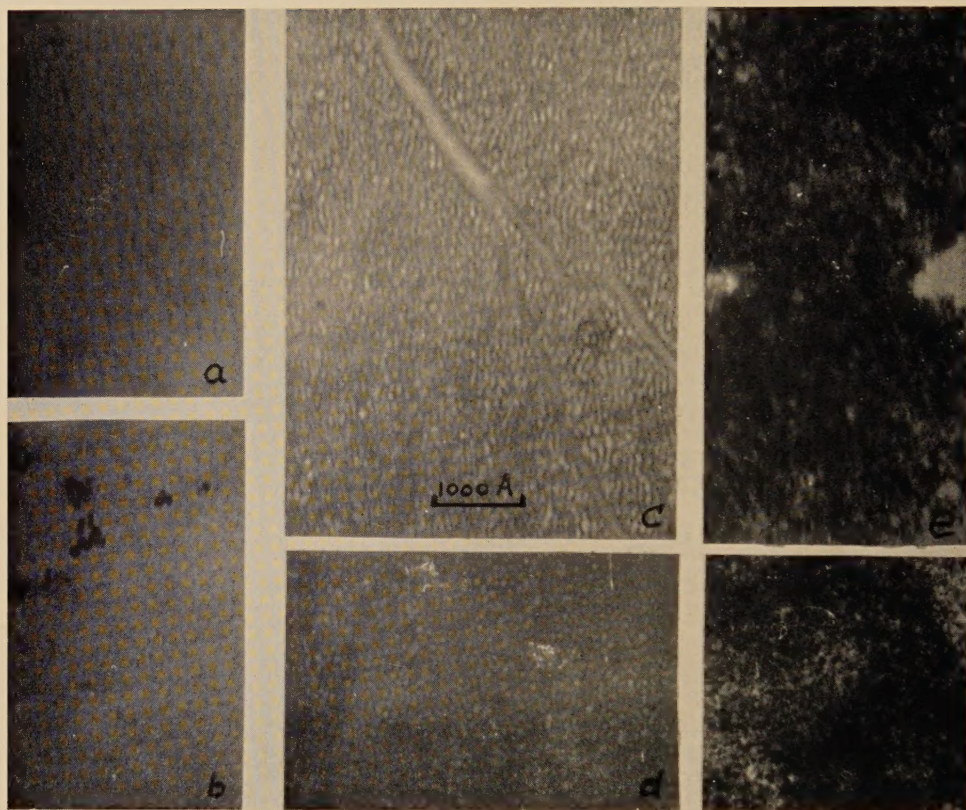


(*b*)

Electron microscope pictures of Ticonal XX. (*a*) Parallel to aligning field;  
(*b*) perpendicular to aligning field. From de Jong *et al.* (1958).



Fig. 7.3



Structure of precipitates in Alnico V. (a), After cooling without controlled rate; (b), after magnetic annealing; (c), after optimum treatment, i.e. (b) + 600°C tempering (longitudinal section); (d), as (c), but cross section; (e), colloid distribution on Alnico V (longitudinal section); (f), as (e), but cross section. From Kronenberg and Tenzer (1958); reproduced from original photographs kindly supplied by the authors.

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